

PRESSURE - VOLUME - TEMPERATURE RELATIONSHIPS OF REFRIGERANT 500 GAS

by
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Ph. D.

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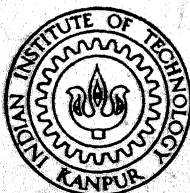
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**DEPARTMENT OF MECHANICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR
MAY, 1976**

PRESSURE - VOLUME - TEMPERATURE RELATIONSHIPS OF REFRIGERANT 500 GAS

A Thesis Submitted
In Partial Fulfilment of the Requirements
for the Degree of
DOCTOR OF PHILOSOPHY

by
MITHILESHWAR PRASAD

to the
**DEPARTMENT OF MECHANICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR
MAY, 1976**

TO

MY PARENTS

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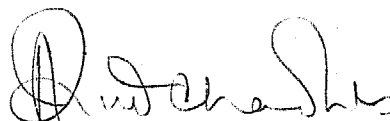
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Certified that the present work, 'PRESSURE-VOLUME-TEMPERATURE RELATIONSHIPS OF REFRIGERANT 500 GAS', has been carried out under my supervision and that this has not been submitted elsewhere for a degree.

May , 1976



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POST GRADUATE OFFICE
This thesis has been approved
for the award of the Degree of
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NOMENCLATURE

Capital Letters

APG	Air piston gauge
B_p	Berlin second virial coefficient, $(\text{Bar})^{-1}$
B_v	Lieden second virial coefficient, (m^3/mole)
C_p	Berlin third virial coefficient, $(\text{bar})^{-2}$
C_v	Lieden third virial coefficient, $(\text{m}^3/\text{mole})^2$
D_p	Berlin fourth virial coefficient, $(\text{bar})^{-3}$
D_v	Lieden fourth virial coefficient, $(\text{m}^3/\text{mole})^3$
DPIA	Differential pressure indicator just outside the bath
DPIB	Differential pressure indicator with dead weight gauge
DWG	Dead weight gauge
G	Gibbs energy, J mole^{-1}
H	Enthalpy, J mole^{-1}
N	Cell constant
P	Pressure
P_r	Pressure after r th expansion
R	Gas constant

Mole denotes g mole (gram mole).

S	Entropy, $\text{JK}^{-1} \text{mole}^{-1}$
T	Temperature
V_I	Volume of chamber I
V_{II}	Volume of chamber II
V_a	Total volume of the sample gas outside the bath
Z	Compression factor

Small Letters

d	Total derivative
f	Fugacity
g	Local gravity
g_s	Standard gravity
n	Number of moles
v	Volume, m^3/mole
x	Mole fraction

Subscripts

i	Integer counter, $i = 1, 2, 3, \dots$
r	Number of expansions
P	Constant pressure
v	Constant volume

Superscripts

o	Property of the substance in its standard state
---	---

Greek Letters

∂	Partial derivative
Δ	Difference
γ	Fugacity coefficient
ϕ	Ratio of number of moles

SYNOPSIS

A Burnett-type apparatus was fabricated and used to obtain compression factors of Refrigerant 500 gas at temperatures 298.15 K and from 313.15 to 413.15 K at 20 K intervals and at pressures below the saturation pressure at each temperature. Refrigerant 500 is a minimum boiling azeotrope of 26.2 weight % of 1,1-difluoroethane (Refrigerant 152a) and 73.8 weight % of difluorodichloromethane (Refrigerant 12). Recent applications of the minimum boiling azeotropes to the vapour compression refrigeration systems have indicated their superiority over their pure constituents under identical conditions.

Pressures were measured by a Ruska dead weight gauge above 3 bars and by a Ruska air piston gauge below .2 bars. Temperatures in the cell and in the constant temperature bath were measured by chromel-constantan thermocouples calibrated against a 25 ohm platinum resistance thermometer and a resistance bridge assembly.

The cell constant, N , was determined by using data on high purity helium.

The overall accuracy of measurements in the compression factors was estimated to be 0.1% or better over the range

of the pressures and temperatures investigated. An elaborate graphical smoothing procedure was followed to obtain smoothed and internally consistent values of compression factors. The differential pressure indicator, the pressure balancing device, was kept at 298.15 K outside the constant temperature bath containing the Burnett cell. Hence at temperatures other than 298.15 K, a correction had to be applied to the measured compression factors.

The only literature P , v , T data for Refrigerant 500 gas is reported by Sinka and Murphy which extend from 322 to 478 K and from 14 to 58 bars. The emphasis in the present investigation has been on the low pressure P , v , T data extending upto about 0.2 bars primarily to obtain reliable values of the second virial coefficients.

The corrected compression factors were used to compute the virial coefficients and the departure functions, that is, the difference between the real gas and the ideal gas properties. The required ideal gas thermodynamic properties for Refrigerant 500 are reported.

CHAPTER I

INTRODUCTION

The accurate determination of the pressure, volume, temperature relationship of a gas over a wide range of pressure and temperature provides important information about the gas from fundamental as well as applied point of view. Knowledge of the equation of state of a gas permits calculation of the dependence of the real gas thermodynamic properties on pressure and temperature, and also provides information about interactions at the molecular level (1,2). The thermodynamic properties, such as, enthalpy, entropy, etc., as functions of pressure and temperature are required in the design of varied engineering systems. The accuracy of the design depends upon the accuracy of the data used in these calculations. It is therefore necessary to know the equation of state of a gas with sufficient accuracy.

The equation of state data are conveniently represented by the compression factor, Z , defined as,

$$Z = \frac{PV}{nRT} \quad (1)$$

Normally, P and T can be measured with high precision and accuracy. Hence, the accuracy of Z is limited by the

accuracy of measurements of n and V , which are difficult to measure. Therefore, it would be desirable to eliminate these difficult measurements of one (n) or both (n and V) variables in establishing the equation of state. The Burnett method (3) provides isothermal pressure measurements before and after stepwise expansions between two volumes and dispenses with the measurements of n and V . This method can, in principle, lead to more accurate values of Z than can be obtained from a method requiring the measurement of each variable in Equation (1). The major disadvantage of this method is the wide spacing of the data points at high pressures and the relatively close spacing at low pressures. This is partly overcome by making more than one run starting with a different initial pressure each time.

The purpose of the present investigation was: (a) to fabricate a Burnett apparatus for the accurate determination of the compression factors for gases and (b) to measure accurate P, v, T data for Refrigerant 500. Refrigerant 500 is a minimum boiling azeotrope of 26.2 weight % of 1,1-difluoroethane (Refrigerant 152a) and 73.8 weight % of difluorodichloromethane (Refrigerant 12) (4).

Recent applications of minimum boiling azeotropes to the vapour compression refrigeration systems have indicated their superiority over their pure constituents

under identical conditions (5,6). While retaining the merits of pure component refrigerants, the use of minimum boiling azeotropes has resulted in increased capacity, attainment of lower temperatures, and as a consequence improved coefficients of performance. The boiling temperature of R 500 (Refrigerant 500) at atmospheric pressure is 239.82 K as compared to 243.36 K for R 12 (Refrigerant 12) and 248.45 K for R 152a (Refrigerant 152a) (7,8). For standard condition of 258.15 K evaporator temperature, the refrigeration capacity of R 500 is 22 percent more than that of R 12 (7). The trend of increasing capacities of conventional plants on the one hand and the use of special purpose equipment on the other, necessitates the search for compounds which will improve the overall performance of the refrigeration system for particular applications. Once such a compound is found, it becomes imperative to know its thermodynamic properties accurately for its best utilisation in the existing systems or to design new ones (9,10,11).

The only literature P , v , T data for Refrigerant 500 are reported by Sinka and Murphy (12), which extend from 322 to 478 K, 14 to 58 bars, and 17×10^{-3} to 149×10^{-3} m³/gm mole. These authors used constant volume type apparatus to measure the P , v , T data and fitted these data to the Martin-Hou equation of state. The data are mainly at high pressures.

Morsy (13) used these data to calculate the thermodynamic properties of R 500.

In the present investigation, P, v, T data for R 500 have been measured from 298.15 to 413.15 K. The pressures at each temperature extended from about half the saturation pressure to 0.2 bars to avoid adsorption effects (14). Pressures were measured by a Ruska dead weight gauge above 3 bars and by a Ruska air piston gauge below 2 bars. Temperatures in the cell and in the constant temperature bath were measured by chromel-constantan thermocouples calibrated against a .25 ohm platinum resistance thermometer and a resistance bridge assembly. The emphasis in this work, has been on the low pressure P,v,T data primarily to obtain reliable values of the second virial coefficients and to extend the range of existing P,v,T data on R 500 in the low pressure region.

In order to obtain reliable results by the Burnett method, it is necessary that the cell constant, N , defined by the ratio $(V_I + V_{II})/V_I$ in the limit as the pressure goes to zero, is determined accurately. In recent years, a number of articles have been published in the literature (15-26) featuring various methods for reducing the experimental data to yield precise and consistent values of N , the compression factors, and the virial coefficients. N , is normally

determined by carrying out pressure measurements to sufficiently low pressures on an inert gas such as helium and this value is assumed to remain constant over a period of time.

In recent years, it has been suggested to determine the cell constant from each series of pressure measurements with the experimental gas itself (16,27). Both these methods have been attempted for the determination of N in the present investigation. It was however felt that the determination of N with the helium data is to be preferred because helium gives a linear pressure ratio versus pressure plot upto moderately high pressures making the extrapolation to zero pressure more reliable.

The experimental data have been used to compute the compression factors, the virial coefficients, and the thermodynamic properties of the real gas for the temperature and pressure ranges investigated.

CHAPTER II

THEORY

The Burnett apparatus basically consists of two chambers of unspecified volume, the sample volume V_I and an expansion volume V_{II} , connected by a suitable valve, the expansion valve. The two volumes are connected to the pressure measuring system, charging system, and the vacuum system as shown in Fig. 1.

The sample volume V_I includes the tubing volume from V_I up to valves 1, 2, and 4. V_a is the volume of the tubing from valve 4 to the Differential Pressure Indicator (DPI) plus the lower side volume of the DPI itself. Normally V_I includes V_a if they are both maintained at the same temperature.

A. Let us assume that V_I , V_{II} and V_a are all maintained at the same constant temperature.

The experimental procedure involves the following sequence of steps in making the pressure measurements at each isotherm. The equation of state for each step is also reported.

Differential pressure
indicator (DPI)

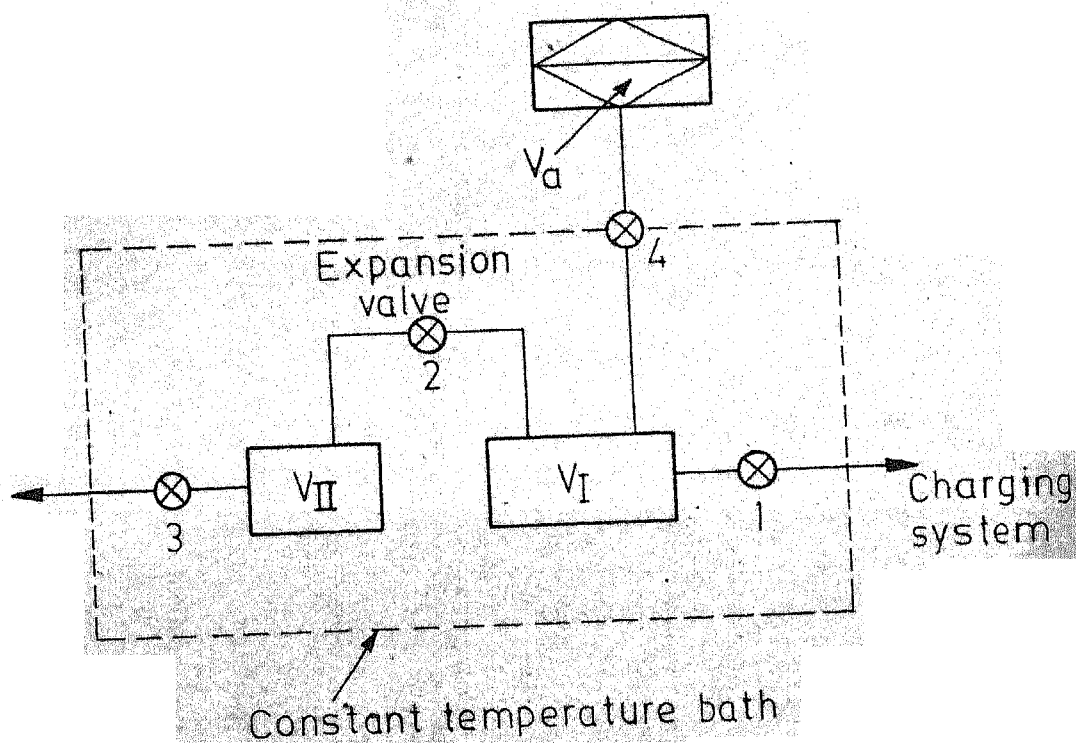


Fig. 1 - The Burnett cell.

a. V_I , V_a and V_{II} are evacuated, the expansion valve is closed, and a quantity of experimental gas is charged in $V_I + V_a$.

$$Z_0 = P_0 \left[V_I(P_0) + V_a(P_0) \right] / n_1 RT \quad (2)$$

Here n_1 represents the initial number of moles, $V_I(P_0)$ and $V_a(P_0)$ indicate that the volumes are pressure dependent as a result of distortion under pressure.

b. Expand into V_{II} . At equilibrium,

$$Z_1 = P_1 \left[V_I(P_1) + V_a(P_1) + V_{II}(P_1) \right] / n_1 RT \quad (3)$$

c. Close the expansion valve and evacuate V_{II}

$$Z_1 = P_1 \left[V_I(P_1) + V_a(P_1) \right] / n_2 RT \quad (4)$$

d. Expand into V_{II}

$$Z_2 = P_2 \left[V_I(P_2) + V_a(P_2) + V_{II}(P_2) \right] / n_2 RT \quad (5)$$

These individual steps are repeated to successively lower pressures with successively smaller quantities of gas that remain in $V_I + V_a$ after each expansion until the lowest pressures, that can be measured both accurately and precisely, are reached.

The equations of state before and after the expansion yield the following relations [using Equations (4) and (5)]

$$P_1(V_I + V_a)/P_2(V_I + V_a + V_{II}) = Z_1/Z_2 \quad (6)$$

$$\text{or } P_1/P_2 = \left[(V_I + V_a + V_{II})/(V_I + V_a) \right] (Z_1/Z_2) \quad (7)$$

Let N_2 be the cell constant for the second expansion as given below:

$$N_2 = (V_I + V_a + V_{II})/(V_I + V_a) \quad (8)$$

The generalised form of Equation (7) for the r th expansion is,

$$\frac{P_{r-1}}{P_r} = N_r (Z_{r-1}/Z_r) \quad (9)$$

The zero-pressure cell constant N is defined as follows:

$$N = \lim_{P_{r-1} \rightarrow 0} (P_{r-1}/P_r) \quad (10)$$

Hence N may be computed by extrapolating a plot of (P_{r-1}/P_r) versus P_{r-1} to $P_{r-1} = 0$.

Equation (9) forms the basis for calculating the compression factors from the pressure ratios. Applying Equation (9) repetitively to the first r expansions, the resulting equations can be combined to give,

$$P_r N^r = Z_r (P_o/Z_o) \quad (11)$$

A plot of $P_r N^r$ versus P_r should extrapolate to (P_0/Z_0) , the run constant at zero pressure. Once (P_0/Z_0) is determined, the compression factors are calculated by rearranging Equation (11) as follows:

$$Z_r = P_r N^r / (P_0/Z_0) \quad (12)$$

Since the cell constant N is raised to the r th power, and $N > 1$, it is apparent that an accurate determination of N is required to obtain reliable values of the compression factors with the Burnett apparatus. Moreover, in the determination of both N and (P_0/Z_0) , extrapolation to zero pressure is involved and this is facilitated with sufficiently accurate and abundant low pressure measurements extending well below one bar. Modern measurements extend to much lower pressures than were possible in the past due to the availability of low pressure piston gauges with high accuracy and reproducibility.

In the conventional determination of N , an inert gas such as helium is used which yields a straight line plot of (P_{r-1}/P_r) versus P_{r-1} and the extrapolation to zero pressure is more reliable yielding a truer value of N . In this procedure it is implied that the distortion of the volumes under the experimental pressures is insignificant meaning thereby that N is a all time constant. This may be true if

the highest experimental pressures are in the range of 20 to 25 bars at which pressures the volume distortion is of the order of 0.004 percent (28).

Hence, depending upon the experimental pressures, the method of treatment of the Burnett raw data is a source of uncertainty in the compression factors. In recent years various improved methods have been proposed in the literature for the treatment of the Burnett data as reported in Chapter I. Most of the improvements are concerned with the analytical procedures which produce simultaneously the cell constant and the virial coefficients consistent with the data.

In the present investigation, the highest pressures involved are in the range of 7 to 8 bars. The volume distortion per 100 bars is calculated to be 0.022 percent at 298.15 K. This distortion in volumes will produce a maximum uncertainty of 0.044 percent at 100 bars in the cell constant N . This uncertainty would be of the order of 0.004 percent in the present situation (maximum pressures of 20-21 bars). From carefully collected data, the graphical procedure yields the value of N within 0.01 percent. Hence the pressure effects on N are insignificant. In the present analysis the graphical procedures are adopted.

Using the graphical procedure N may be determined by treating the helium data at each experimental isotherm or by

treating the data on experimental gas itself at each isotherm. The former procedure implies that N is constant over the entire period of experimentation which may not be true. Some investigators, therefore, propose that it is advisable to determine N by the latter procedure. The difficulty of obtaining N with the experimental gas is that the plot of (P_{r-1}/P_r) versus P_{r-1} is not linear specially at lower pressures making extrapolation to zero pressure difficult and uncertain. In the present investigation, N was determined by using the Helium data.

B. Let us now assume that V_a is kept outside the constant temperature bath i.e. V_I and V_{II} are placed in the bath and V_a is at a temperature T_a , say 298.15 K. Let V_I and V_{II} be at temperature T . With this arrangement a small fraction of the experimental gas charged in $V_I + V_a$ and contained in V_a is at T_a while most of it is in V_I at T . Though V_a is considerably smaller than V_I ($V_I/V_a \approx 200$), such an arrangement will yield wrong compression factors. Hence a correction (henceforth referred to as the DPI correction) is necessary to obtain the correct compression factors and the procedure is given below:

a. Charge n_1 moles of gas in $V_I + V_a$ at temperature T .

$$n_1 = \frac{P_o V_I}{Z_o RT} + \frac{P_o V_a}{Z_{oa} RT_a} \quad (13)$$

b. Expand into evacuated V_{II}

$$n_1 = \frac{P_1 (V_I + V_{II})}{Z_1 RT} + \frac{P_1 V_a}{Z_{1a} RT_a} \quad (14)$$

Here, $Z_O(P_O, T)$, $Z_{Oa}(P_O, T_a)$, $Z_1(P_1, T)$, $Z_{1a}(P_1, T_a)$.

From Equations (13) and (14)

$$\frac{P_O V_I}{Z_O RT} + \frac{P_O V_a}{Z_{Oa} RT_a} = n_1 = \frac{P_1 (V_I + V_{II})}{Z_1 RT} + \frac{P_1 V_a}{Z_{1a} RT_a} \quad (15)$$

Define,

$$\phi_1 = \frac{\text{moles in } (V_I + V_a + V_{II}) \text{ at } P_1}{\text{moles in } (V_I + V_a) \text{ at } P_1} \quad (16)$$

Moles in $(V_I + V_a + V_{II})$ at P_1

$$= \frac{P_1 (V_I + V_{II})}{Z_1 RT} + \frac{P_1 V_a}{Z_{1a} RT_a} \quad (17)$$

Moles in $(V_I + V_a)$ at P_1

$$= \frac{P_1 V_I}{Z_1 RT} + \frac{P_1 V_a}{Z_{1a} RT_a} \quad (18)$$

From Equations (16), (17), (18) and rearranging,

$$\phi_1 = \frac{\left(\frac{V_I + V_{II}}{V_a} \right) \left(\frac{Z_{1a}}{Z_1} \right) \left(\frac{T_a}{T} \right) + 1}{\left(\frac{V_I}{V_a} \right) \left(\frac{Z_{1a}}{Z_1} \right) \left(\frac{T_a}{T} \right) + 1} \quad (19)$$

$$\text{Let } \tau_1 = \left(\frac{Z_{1a}}{Z_1} \right) \left(\frac{T_a}{T} \right) \quad (20)$$

Hence,

$$\phi_1 = \frac{\left(\frac{V_I + V_{II}}{V_a} \right) \tau_1 + 1}{\left(\frac{V_I}{V_a} \right) \tau_1 + 1} \quad (21)$$

c. Evacuate V_{II} . n_1/ϕ_1 moles of gas are left in $V_I + V_a$ at P_1 .

$$\frac{n_1}{\phi_1} = \frac{P_1 V_I}{Z_1 RT} + \frac{P_1 V_a}{Z_{1a} RT_a} \quad (22)$$

d. Expand into V_{II} :

$$\frac{n_1}{\phi_1} = \frac{P_2 (V_I + V_{II})}{Z_2 RT} + \frac{P_2 V_a}{Z_{2a} RT_a} \quad (23)$$

From Equations (22) and (23),

$$\phi_i = \frac{\left(\frac{V_I + V_{II}}{V_a}\right) \tau_i + 1}{\left(\frac{V_1}{V_a}\right) \tau_i + 1} \quad (28)$$

and,

$$\tau_i = \left(\frac{Z_{ia}}{Z_i}\right) \left(\frac{T_a}{T}\right) \quad (29)$$

If V_a were inside the bath, then $\phi = N$, the cell constant, and Equation (27) is equal to Equation (11).

C. Calculation of 'correct' compression factors from the experimental Burnett data with V_a outside the bath and at $T_a = 298.15$ K:

It is assumed that experimental compression factors at $T_a = 298.15$ K are measured (no DPI correction is involved at T_a) and also the values of (V_I/V_a) and $(V_I + V_{II})/V_a$.

1. At $T \neq T_a$, use the experimental pressure sequence $P_0, P_1, P_2, \dots, P_r$ to calculate a first-order approximation of the compression factors $Z_0, Z_1, Z_2, \dots, Z_r$ from the standard Burnett calculation procedure, that is ignoring the DPI correction.

2. To calculate the 'correct' compression factors:
 - a) Assume the above value of Z_0 and calculate Z_1 using Equation (15).
 - b) Calculate ϕ_1 using Equation (19).
 - c) Calculate Z_2 from Equation (24).
 - d) Calculate ϕ_i , Z_i values for the remaining pressures, from Equations (26), (28), and (29).
 - e) We now have the sequences Z_0 , Z_1 , Z_2 , ..., Z_r and ϕ_1 , ϕ_2 , ..., ϕ_{r-1} .
 - f) Note that this compression factor sequence obtained in e) will not exactly agree with that obtained in (1) above.
 - g) Plot Z_i versus P_i or fit the data to a polynomial in P and extrapolate to $P = 0$.
 - h) Check if $Z = 1$ at $P = 0$.
 - i) If $Z > 1$ at $P = 0$, start 2a with lower value of Z_0 and repeat calculations from 2a to 2h.
 - j) If $Z < 1$ at $P = 0$, start 2a with higher value of Z_0 and repeat calculations from 2a to 2h.
 - k) The 'correct' sequence of the compression factors Z_0 , Z_1 , Z_2 , ..., Z_r is thus obtained if 2h is satisfied within the stated limits of Z ($\Delta Z \leq 0.0001$).

CHAPTER III

EXPERIMENTAL APPARATUS

The Burnett apparatus used in this investigation was basically similar in design to that used by Anderson (29) and others (30-47), with some important modifications. A schematic diagram of the apparatus is shown in Fig. 2.

For the purposes of detailed description, the apparatus may be divided into the following sections:

- A. The compressibility cell
- B. The constant temperature bath
- C. The vacuum system
- D. The charging system
- E. Temperature measurement.
- F. Pressure measurement.

A. The Compressibility Cell

The compressibility cell is the heart of the Burnett apparatus and is designed uniquely for this type of experiment. A line drawing describing the basic design is shown in Fig. 3(a). The cell itself was machined from Type 316 stainless steel. The finished cell was 0.1 m O.d. by

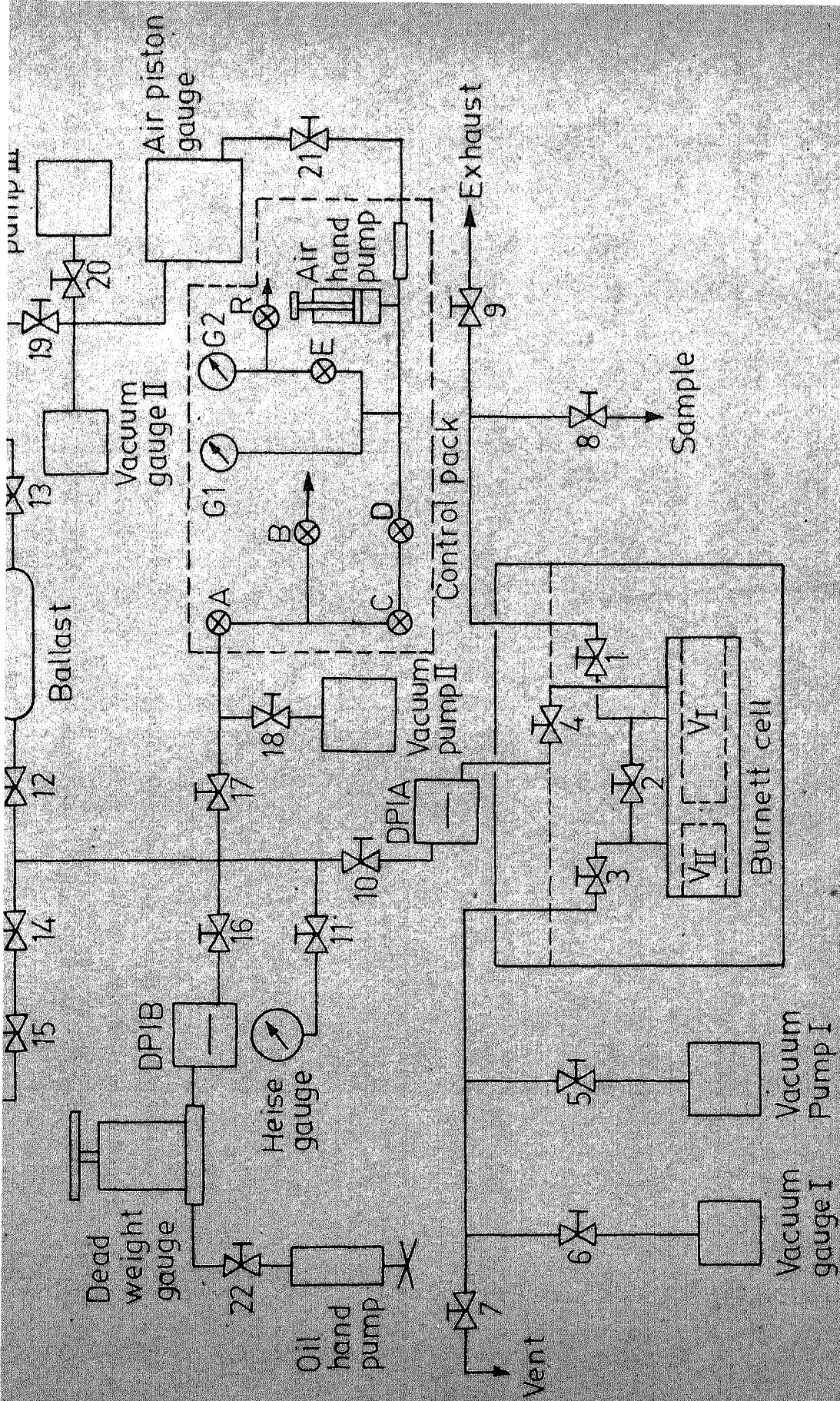
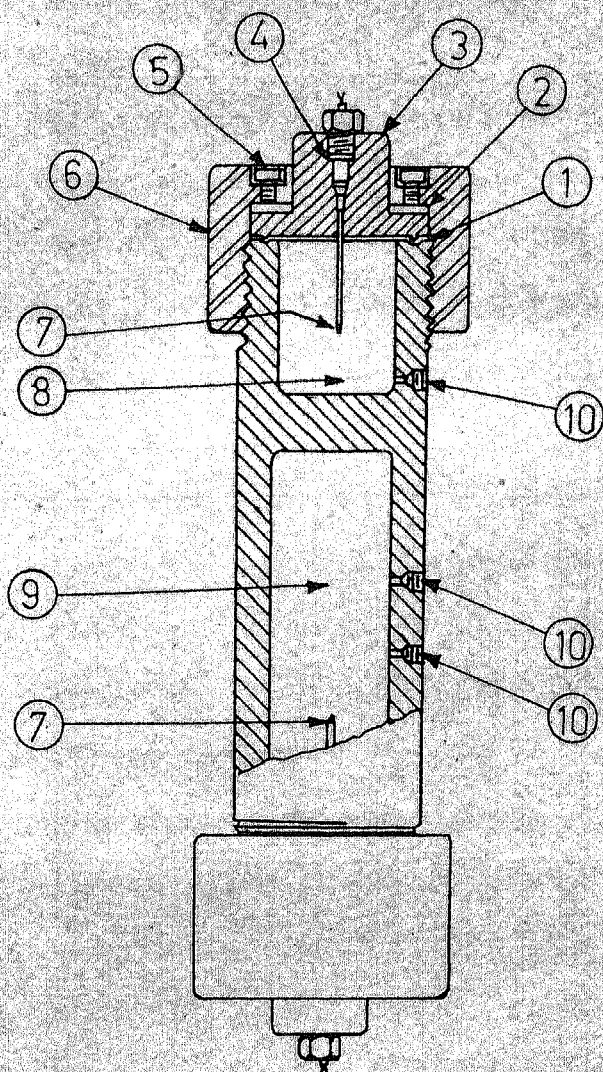
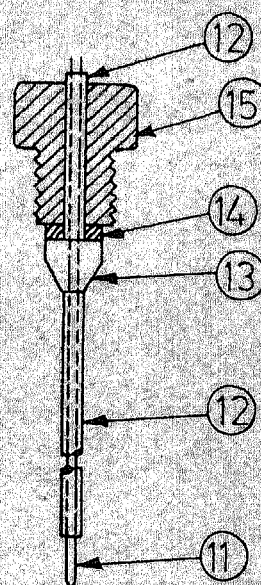


Fig. 2 - Schematic diagram of the Burnett apparatus.



(a) Compressibility cell.



(b) Thermocouple packing assembly.

Head gasket

Cap screw ring

Head

Thermocouple packing assembly

Cap screw

Cap

Thermocouple junctions

Chamber II

(9) Chamber I

(10) Pressure connections

(11) Thermocouple wires

(12) Ceramic insulators

(13) Teflon packing

(14) S.S. washer

(15) Packing nut

Fig. 3.

0.38 m long. The sample chamber V_I , 0.06 m i.d. by 0.245 m long (approximate volume, $883 \times 10^{-6} \text{ m}^3$), and the expansion volume V_{II} , 0.06 m i.d. by 0.105 m long (approximate volume, $380 \times 10^{-6} \text{ m}^3$), were bored from opposite ends of the cell block. Eubank and Kerns (48) in their recent analysis of adsorption and molecular association in the Burnett apparatus have recommended the following modifications: (a) Type 303 stainless steel for construction of the compressibility cell should be avoided as it gives a poor finish and consequently leads to adsorption (14), (b) the elimination of usual tapers at the bottom of V_I and V_{II} (29, 31), and (c) the surface of the cell be superfinished. These modifications have been incorporated in the present design of the apparatus. In our case an excellent finish of the cell surface was obtained by special lapping process provided at the Indian Ordnance Factory, Kanpur. Unfortunately the surface finish could not be measured due to nonavailability of proper instrument having the required precision.

Closure of the two volumes was accomplished by heads made of Type 316 stainless steel. A V-shaped bead with fine circular end was machined on the flange of the head and a matching groove was made on the cell. An annealed and polished copper gasket of nearly 0.0005 m thickness formed the seal between the cell and the head. The height of the bead

was kept approximately 0.0005 m more than the depth of the groove to achieve a line contact. The heads were held in place by caps machined from cold-rolled steel. A hardened steel ring of 0.004 m thickness separated the head and twelve cap screws of 0.009525 m size threaded through the steel cap. The cell assembly was designed for an operating pressure of 276 bars. The effect of internal pressure on the volume of either chamber was calculated according to the relations given by Comings (28) for thick-walled cylinders. At 298.15 K, the change in volume is approximately 0.022 percent per 100 bars internal pressure.

Pressure connections to the cell were designed to use high pressure cone fittings of the Autoclave Engineers (49). These connections were of the female type and required a 60 degree conical seat.

The thermocouple packing assembly as shown in Fig. 3(b) was used to insert thermocouples in volumes V_I and V_{II} for the temperature measurement. The thermocouples were directly exposed to the experimental gas. Stainless steel nuts pressurised the teflon packing (Conax Corporation, USA) of tapered shape to matching seats in the two heads through stainless steel collars. Enamelled chromel-constantan thermocouples of 24 gauge size entered the cell through the packing. Appropriate torque applied to the nuts prevented

the possibility of any leak through the packing assembly. Cylindrical ceramic insulators (Conax Corporation, USA) with two axial holes were provided on both sides of the teflon packing so that thermocouple wires do not come in contact with each other or with the cell head and packing nut walls. The thermocouple wires were provided with ceramic beads upto the liquid level in the bath after which plastic insulation was put over them.

Four 0.003175 m stainless steel high temperature needle valves 1, 2, 3, and 4 supplied by Autoclave Engineers Inc, with teflon packing, were used as shown in Fig. 2. Valve 1 served as the charging valve and was opened only to supply the sample gas at the start of each run. Valve 2, the expansion valve, connected the two volumes V_I and V_{II} . Unfortunately a constant volume valve could not be obtained in time. Valve 3 served as the exhaust valve and connected the cell to the vacuum system through volume V_{II} . The sample chamber V_I was linked with the differential pressure indicator, DPIA, through valve 4 for pressure measurement. We were not successful in obtaining a high temperature differential pressure indicator (DPI) which could be placed inside the bath. Hence the DPI had to be placed outside the bath under controlled temperature of 298.15 K. This is a source of error which could not be avoided. The error is corrected

by applying the DPI correction procedure as explained in Chapter II.

B. The Constant Temperature Bath

A rectangular bath of size 0.7 m x 0.45 m x 0.5 m was constructed from stainless steel sheet of 0.001 m thickness. Six numbers of 0.0127 m O.d. stainless steel tubes were welded to the bath, 0.05 m above the bottom, to accommodate the tubular heaters. These tubes ran along the length of the bath, were equidistant, and projected 0.08 m on both the sides. The bath was reinforced from outside with slotted angle iron so closely that there was no trace of any bulge when filled with water upto the brink. A 0.05 m thick glass wool insulation was provided from all the four sides and at the bottom of the bath. Finally the bath was covered with a thin aluminium sheet.

The bath liquid, Teresso-56, supplied by Hindustan Petroleum Company (Bombay), was maintained at a level 0.05 m below the top of the bath. Efficient stirring was provided by a 0.18639 watt, 4000 rpm stirrer (Remi Udyog, Bombay). The stainless steel stirrer shaft, 0.0127 m dia by 1.07 m long, had provision for movement in all the three directions. It entered the bath from the top, parallel to the longer side at about an angle of 45 degree with the vertical. Two

0.075 m stainless steel propellers were used. One was connected to the shaft, approximately 0.1 m below the surface of the bath liquid, and the second was attached to its end, nearly 0.15 m above the bottom of the bath. This arrangement provided for a continuous turnover of bath liquid and allowed minimum dead space.

The compressibility cell was placed in the middle of the bath, 0.12 m above the bottom, through an overhead structure consisting of rigidly fixed mild steel pipes and strips. Valves 1,2,3, and 4 were tightly held in place with the help of the mounting brackets. A hydraulic jack, firmly established below the ground level, raised and lowered the bath, when necessary. In upper and lower positions, the bath was supported on a very strong structure of teak wood reinforced with slotted angle iron. This structure was capable of quick assembly and disassembly and made the raising and lowering operation of the bath much easier. The working position of the bath was such as to facilitate easy access to all the components which need control, including the contact thermometer and valves, while standing at the ground level. With this arrangement the cell and its connections were not disturbed whenever a problem arose. Valves 1,2,3, and 4 carried extended stems of 0.00635 m dia stainless steel rod so that they could be operated from outside the bath. All tubing was 0.00635 m o.d. by 0.003175 m i.d. stainless steel high pressure tubing.

C. The Vacuum System

The vacuum system consisted of vacuum pump I (Precision Scientific Company, USA) to evacuate the cell and a Pirani gauge ('Hind Hivac' Company, India), vacuum gauge I, to measure the pressure below one bar in the system (Fig.2). Vacuum pump I was connected to the expansion volume V_{II} through valves 5 and 3. The use of valve 5 prevented the high pressure exhaust gas from entering into vacuum pump I. Valve 6 performed the same job for vacuum gauge I. Venting and exhaust purposes were served by valve 7.

All tubing was 0.00635 m O.d. by 0.003175 m i.d. stainless steel high pressure tubing and valves 5, 6, and 7 were 0.003175 m stainless steel Hoke needle valves.

This system reduced the pressure in the expansion volume V_{II} to 5×10^{-6} bars in about 10 minutes and was capable of outgassing the entire compressibility cell to 2×10^{-6} bars.

D. The Charging System

The charging system for this investigation was rather simple since the highest working pressure was lower than the vapour pressure of the sample gas at room temperature.

The charging cylinder was connected to the sample chamber V_I through valves 8 and 1. The use of valve 8 helped in allowing lesser moles of gas to enter V_I at any time. Valve 9 helped in obtaining an approximately predetermined pressure at the start of a particular run.

E. Temperature Measurement

Temperatures were measured with chromel-constantan thermocouples (Thermoelectric Co., USA) as they have good stability and give highest emf output as compared to other common thermocouples (50, 51). The emf was measured by a Type K-3 Universal Potentiometer (Leeds and Northrup Company, Ser. No. 1630194) and a Leeds and Northrup 2430 DC Galvanometer (Ser. No. 1632348) assembly. An Eppley Standard Cell (unsaturated type) and two dry cells (No. 6 type) made the arrangement complete. Four thermocouples were used; two were placed in the cell through thermocouple packing assembly as shown in Fig. 3(b), the third was located inside the oil bath near the compressibility cell, and the fourth, a movable one, was used to check the temperature gradient inside the bath. The reference junction used was a homogeneous mixture of finely powdered ice and water contained in a thermos flask. By means of a selector switch (Leeds and Northrup Company), each of the four thermocouple junctions were put separately in series

the reference junction. The temperature measurement and control system is shown in Fig. 4.

All the thermocouples used in this work were calibrated with a 25 ohm platinum resistance thermometer (Leeds and Northrup Company, Ser. No. 1781311), a Leeds and Northrup thermometer bridge (Ser. No. 1776233), and a Leeds and Northrup 2430 DC Galvanometer (Ser.No.1637604), assembly. The calibration of the thermocouples is reported in Appendix A.

The temperature control in the constant temperature bath was accomplished by use of a 'JUMO' (German Democratic Republic) on-off type temperature controller. The sensing element, called the contact thermometer, extended into the bath from the top some 0.03 to 0.04 m away from the control heater and next to the compressibility cell. The contact thermometer of range 273.15 to 423.15 K was electrically connected to the control heater through an electronic relay. Six tubular heaters each of 1000 watt, 110 V capacity were used, enclosed by 0.0127 m stainless steel tubes welded to the bath. All the heaters were supplied power through voltage regulators. One of these heaters was used as a control heater and others were used as constant heat sources, as and when needed.

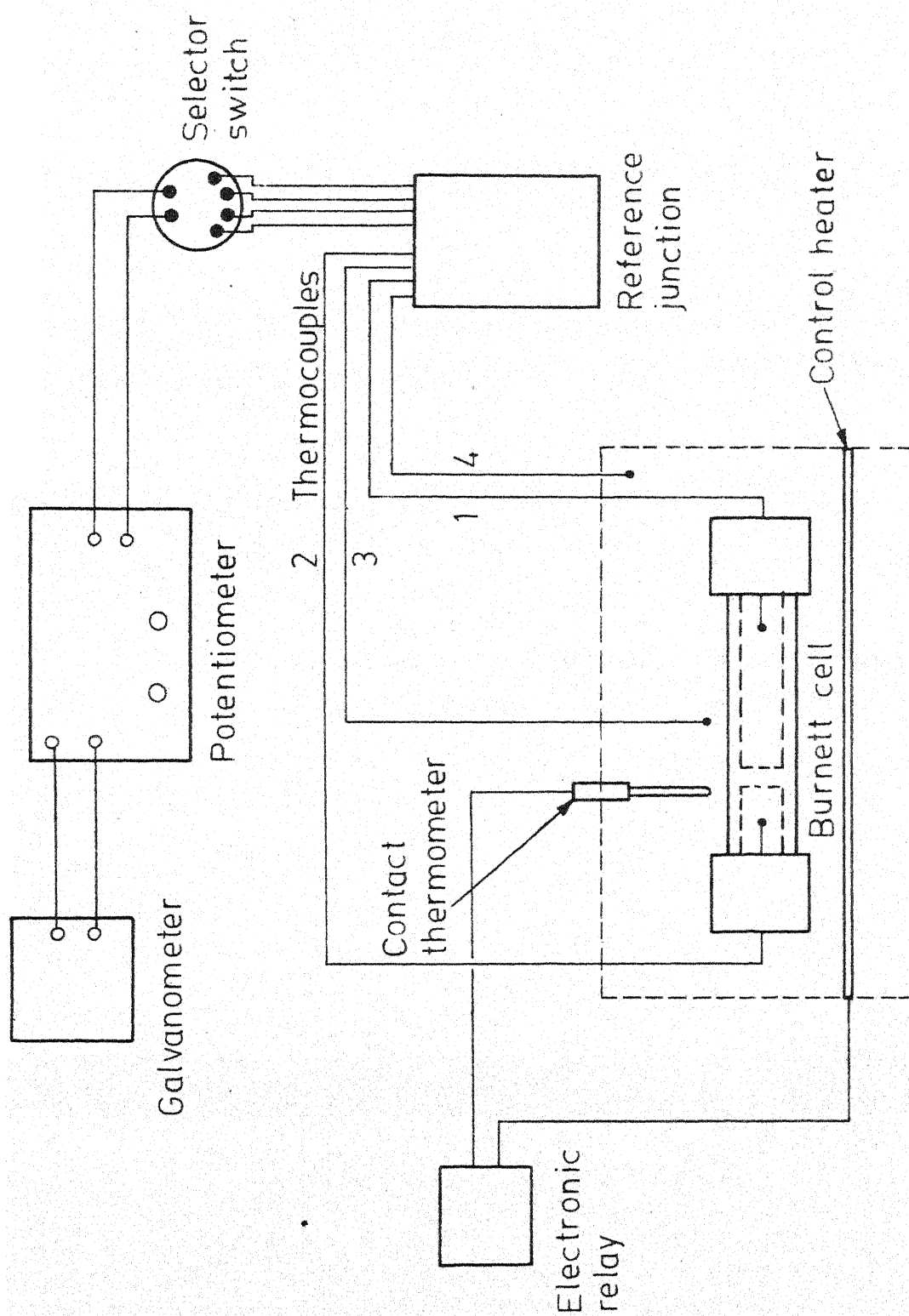


Fig. 4 - Temperature measurement and control system.

In order to control the temperature of the bath at 298.15 K, a small portable cooler (Precision Scientific Company, USA, Ser. No. Z 5) was used. The evaporator coil was immersed in the bath oil, nearer to the stirrer. This arrangement removed the heat of mixing and also ensured enough temperature drop to utilize the control heater.

Volume V_a was enclosed in a well insulated wooden box and its temperature was controlled at 298.15 K throughout the experimentation in the following manner. A 1.5 ton 'Deluxe' room air conditioner (American Refrigerator Co.) maintained the surrounding temperature slightly below 298.15 K by proper setting of its thermostatic switch. A small heater (Sears Co., USA) was placed on the top of the box, with heating element facing volume V_a through an opening. This heater was utilized as a control heater connecting it to a 'JUMO' on-off type contact thermometer through an electronic relay. The temperature inside the wooden box, very close to volume V_a , was measured from time to time with a chromel-Constantan thermocouple and was found to vary within ± 0.1 K.

F. Pressure Measurement

Pressure measurement is the most critical part of the entire operation. This measurement required several delicate and accurate instruments as shown in Fig. 2. Our investigation required a precise pressure balancing device which could be immersed in the oil bath without affecting its accuracy, so that no fraction of the sample gas is subjected to a temperature other than bath temperature. As mentioned earlier, a high temperature DPI (from Ruska Instrument Corporation) could not be obtained for this work. Hence, it was decided to fabricate a mercury differential pressure indicator of the type used by McKetta et al. (1957) for the measurement of pressure in the sample chamber V_I . It was fabricated from a 0.0254 m thick, Type 316 stainless steel plate with the required degree of precision. Numerous problems were faced with this differential manometer in terms of valve seat, leaks, etc., which forced us to abandon this piece of equipment. With great reluctance it was decided to use a Ruska differential pressure indicator, DPIA, with recommended temperature range of 277 to 344 K (50 to 300 °C) which was placed outside the bath for the experimentation (Fig. 2). The DPIA consisted of a differential pressure cell (model 2413; Serial No. 17068) having a very thin stainless steel diaphragm to achieve the pressure balance

on the two sides and an electronic null indicator (model 2416.2) to indicate the above balance of pressures. The sample chamber V_I was connected to the lower side of the differential pressure cell, DPIA, through valve 4, as the volume of the lower cavity ($0.6 \times 10^{-6} \text{ m}^3$) is quite small compared to the upper cavity volume ($29.5 \times 10^{-6} \text{ m}^3$). This cell was kept very close to the constant temperature bath to keep the tubing length minimum from valve 4 to volume V_I . As defined in Chapter II, volume V_a is the sum of the inside volume of the tubing from valve 4 to DPIA and its lower cavity volume. Volume V_a , in our investigation turned out to be $4.3 \times 10^{-6} \text{ m}^3$ approximately. The upper side of the differential pressure cell was connected to the nitrogen line through valve 10. Nitrogen was supplied from a cylinder at about 70 bars through valves 14 and 15. Valve 16 connected a Heise Bourdon tube pressure gauge to the nitrogen line to indicate the approximate experimental pressure. A high pressure ballast was used through valve 17 to minimise the pressure fluctuations of nitrogen during the experimentation. Nitrogen pressure was controlled efficiently with the help of a high precision twenty two turn Hoke needle valve, valve 13.

Once the pressure balance between the sample gas and nitrogen was obtained with the DPIA, the pressure of nitrogen was measured as accurately as possible. Following instruments were used for the measurement of this pressure. A Ruska Model 2400 dead weight gauge (53), Serial Nos. 16921 (gauge) and 16925 (weights), measured the pressure in the range of about 3 to 29 bars. A Ruska Model 2465 air piston gauge (Ser. No. 17383) was used over a pressure range of about 0.14 to 2 bars (54). Unfortunately, these two gauges did not overlap in the pressure range encountered. The instrument calibration constants, calibration of stainless steel weights, and the accuracy of calibration for the dead weight gauge and the air piston gauge are given in Appendices B and C respectively. A Ruska Model 2426 oil hand-pump (Ser. No. 16289), and a Ruska differential pressure null indicator, DPIB, composed of a differential pressure cell (model 2413; Ser. No. 16375) and electronic null indicator (model 2416, Ser. No. 17278), connected to either side of the dead-weight gauge by means of thick walled 0.003175 m O.d. stainless steel tubing completed the high pressure measurement apparatus as shown in Fig. 2. The other side of the differential pressure cell, DPIB, was connected to the nitrogen line through valve 16.

A Ruska Model 2461.1 pressure control pack (Ser. No. 17380), was connected to the air piston gauge through valve 21 on one side and to DPIA through valves 17 and 10 on the other side (Fig. 2). This arrangement provided better regulation of nitrogen pressure for the low pressure measurements. Vacuum pump II, through valve 18, created vacuum in the nitrogen line for pressure measurements below one bar. These pressures were measured with reference to a pressure of 6.8×10^{-4} bars, created by vacuum pump III inside the bell jar of the air-piston gauge. Valve 20 connected the air piston gauge to vacuum pump III. Venting of this pump was accomplished through valve 19. The reference pressure inside the bell jar was measured with a 'Hind Hivac' Pirani gauge, vacuum gauge II.

Atmospheric pressure was read with a mercury barometer with an accuracy of $\pm 6.8 \times 10^{-7}$ bars. The barometer was located inside the laboratory at relatively constant temperature. The atmospheric temperature was measured with a thermometer.

All power supply was made through two, 10 KVA, voltage stabilisers (Aplab, Bombay).

All machining work involved was carried out in the Central Workshop of Indian Institute of Technology, Kanpur.

CHAPTER IV

EXPERIMENTAL PROCEDURE

The compressibility cell and the tubings were thoroughly cleaned with GR grade acetone and then assembled as shown in Fig. 2. The entire set-up was tested for leaks with dry and pure nitrogen. The apparatus was then degassed for 72 hours to ensure that it was completely free of acetone and air. The cell and tubings were then flushed with helium several times. The apparatus was evacuated to about 2×10^{-6} bars over a period of twelve hours. After this, the following step by step procedure was followed to make a run at each isotherm.

A. Attainment of Desired Temperature

The bath liquid was brought to the desired temperature by adjusting the control heater and the auxiliary heaters, and by efficient stirring of the bath liquid. Sufficient time was spent to make sure that the temperature gradient inside the bath liquid was minimum for any particular isotherm with the help of a movable thermocouple 4 (Fig. 4). The readings of the two thermocouples, 1 and 2, in V_I and V_{II} , and that of the thermocouple 3 just outside the

compressibility cell, were recorded after every half hour. When three such consecutive sets of readings showed a maximum difference of 0.008 K between any two temperatures of a set which is well within the accuracy of measurements, it was assumed that the desired temperature has been achieved. For maintaining the bath temperature at 298.15 K, a portable cooler was used and the temperature was maintained accurate to ± 0.01 K. The temperature of volume V_a was maintained at 298.15 K within ± 0.1 K with the help of the room air-conditioner and the control heater provided for this purpose.

B. Nulling of the Differential Pressure Indicators

Before the experimentation was started, the DPIA and DPIB were nulled by opening the top and the bottom sides of both the DPIs to the atmosphere. The needles on both DPIs were brought to zero position by turning the zero adjust knob on the DPIs. The zero setting was checked during the experimentation and did not show any shift until the completion of all experiments.

C. Evacuation

Valves 1 and 7 were closed, and the cell was evacuated by operating pump I and keeping valves 2,3,4,5 and 6 open. Evacuation of the cell was continued until a pressure of 5×10^{-6} bars was obtained. Valves 2,3 and then valves 5

and 6, were closed. Vacuum pump I was vented and shut off.

D. Charging of the Cell With the Sample

The oil side of the DPIB was overpressured by placing a weight load on the dead weight gauge (hereafter referred to as DWG). Valve 17 was kept closed at all times during a high pressure run to avoid damage to the air piston gauge (hereafter referred to as APG). It was opened only when the operating pressure was below 2 bars. Valves 10, 11, 12 and 16 were opened, and compressed nitrogen was allowed to enter in the top side of the DPIA and in the bottom side of the DPIB by slowly opening valves 14 and 15 until the pressure in DPIA was slightly lower than the DWG pressure. It is recommended that the DPIs be overpressured from the same side. Valves 14 and 15 were closed. Because of the higher pressure from the top side of the DPIB, its needle is deflected to the right. The approximate pressure in the system was indicated on the Heise gauge. The system was ready for charging the sample. Volume V_I was charged with the sample by closing valve 2 and opening valves 1 and 8. Charging of the sample had to be done very slowly and it was necessary to check the position of the DPIB needle from time to time. The approximate initial pressure was achieved when the DPIB needle shifted from right to left. Any excess sample was discharged through

valve 9. Valves 1 and 8 were then closed. Charging procedure for all the isotherms remained the same as described above. Valve 4 was kept exactly one eighth turn open throughout the experimentation.

E. Pressure Measurement with the Dead Weight Gauge

The DWG piston with the appropriate weights was floated to its reference level by means of the piston gauge oil injection pump (oil hand pump), and the weight table and the piston assembly was rotated in the clockwise direction by switching on the motor (53).

The DPIA and the DPIB were nulled simultaneously by removing or adding weights from or to the DWG while releasing nitrogen through valve 13 or taking it inside through valves 14 and 15. The DPIs are very sensitive to changes in pressure, therefore, a high pressure ballast was connected in series to the nitrogen line to reduce the pressure changes when nitrogen is taken into or exhausted out of the nitrogen line. Moreover, valve 13 was a high precision needle valve with 22 turns, and hence controlled the nitrogen exhaust very efficiently. During the balancing step, it was necessary to adjust the gauge piston to its reference level from time to time. A precision cathetometer (ELFO, India) with an accuracy of $\pm 10^{-5}$ m was used for this

purpose. The pressure readings were taken when the piston was rotated in the clockwise and counterclockwise directions for a period of five to ten minutes. In general, these two readings differed at most by 2×10^{-4} Kg weight on the piston; therefore, the final pressure was taken as an average of the two readings. The weights on the piston gauge and the temperature of the gauge oil were noted. The stainless steel weights were calibrated by Ruska Instrument Corporation and the calibration is given in Appendix B. The fractional stainless steel weights used were calibrated with a five-place Mettler precision balance and the calibration is reported in Appendix D. A clean tissue paper was used for handling the weights. Smaller weights were handled by forceps with ebonite ends. The pressure corresponding to the particular masses was calculated, and the corrections were made according to the procedure described in the National Bureau of Standards Monograph No. 65 (55). The corrections were made for the gravitational effects, distortion of piston area due to pressure, changes in the temperature, buoyancy of air, and pressure gradients throughout the hydraulic as well as nitrogen system. The atmospheric pressure was accurately measured with a precision barometer and was corrected for temperature (56).

F. Pressure Measurement with the Air Piston Gauge

When the cell pressure fell below 2 bars, the pressure measurement was done with the APG. Before making the measurement, the gauge was adjusted, using the two levelling screws on the front, until the level vial at the motor housing indicated that the gauge was levelled. Valves 11 and 16 were closed and valve 17 was slowly opened. For cell pressures above the atmospheric pressure, valves 18 and 20 remained closed whereas valve 19 remained open throughout. On the control pack side shown with dotted lines in Fig. 2, valves A, D, and E were kept open all the time and valve B was used to exhaust the excess nitrogen when necessary. Valve 21 was closed and valve C was opened slowly. Approximate nitrogen pressure was read on pressure gauge G2, and APG was loaded accordingly by removing the bell jar. The stainless steel weights were calibrated by Ruska Instrument Corporation and the calibration is given in Appendix C. Fractional weights were the same as used for DWG measurements. The air hand pump was adjusted approximately in the centre of the travel. Valve 21 was opened and APG was switched to the clockwise position. With proper manipulation of nitrogen pressure and weights on APG, the piston was floated in between the upper and lower limits. The floating of the piston was assumed when the piston

rotated freely for some time even when the motor was shut off (54). Slow variation of the nitrogen pressure was made with the help of the air hand pump. Sufficient time was spent in the beginning to be able to float the piston without over or under shooting the desired pressure. No change in pressure was observed when the APG was switched to the counterclockwise position. The motor was used only when necessary. Final reading was taken with the bell jar placed in position.

Pressures below the atmospheric pressure were measured with reference to a pressure of 6.8×10^{-4} bars which was produced inside the bell jar by operating vacuum pump III. Valve 19 was closed and valve 20 was kept fully open until vacuum gauge II showed a pressure of 6.8×10^{-4} bars. The DPIA was nulled by creating required vacuum inside the nitrogen line by opening valve 18 and operating vacuum pump II. To start with, approximate weights were placed on the piston of the APG in accordance with the pressure read by pressure gauge G2, which had calibrations below one bar. For each addition and subtraction of the weights on the piston, valve 20 was closed and the bell jar had to be vented through valve 19 such that it could be removed from the APG. Thus, pressure measurements below atmospheric pressure took much more time as compared to the pressure

measurements above atmospheric pressure. The pressure corresponding to the particular masses was calculated, and the corrections were made as described earlier for the DWG readings.

All final pressure readings were taken after the attainment of thermal equilibrium in the cell. Pressure readings were taken after charging and subsequent expansions.

G. Expansion

The expansion of the experimental gas from V_I into V_{II} was achieved by opening expansion valve 2 exactly half turn. Volume V_{II} was already evacuated prior to the charging step. Pressure was measured after the equilibrium was attained. Valve 2 was closed and the pressure reading was taken again. There was no difference between the two pressure readings. Vacuum pump I was started, valve 7 was closed and valves 5 and 6 were opened. At higher pressures before evacuation of V_{II} , part of the sample gas was vented out by closing valves 5 and 6 and opening valves 7 and 3. At pressures below atmospheric pressure, valve 7 was kept closed and valve 3 was opened only when the vacuum gauge I indicated a pressure of about 5×10^{-6} bars. This process eliminated the possibility of any foreign gas

entering into volume V_{II} . Valve 3 was closed only when vacuum gauge I indicated a pressure of 5×10^{-6} bars inside the system. After this, vacuum pump I was vented and shut off. Valve 2 was then opened for expanding the experimental gas into V_{II} . This procedure of evacuation and expansion was continued until a pressure of 0.2 to 0.4 bars was obtained in the cell. The temperature of the bath was checked intermittently while the pressure readings were taken for a run. The step by step procedure outlined above was then followed to make another run.

After the helium runs were over, the complete cell assembly including the charging line was thoroughly evacuated for 48 hours to a pressure below 2×10^{-6} bars. Then, the experimentation was carried out with R 500, after flushing the cell three to four times with it, exactly in the same manner as described for helium.

H. Determination of the Ratio V_I/V_a

The ratio V_I/V_a at 298.15 K was determined experimentally by making helium runs in the following manner.

The entire compressibility cell was evacuated to a pressure of 5×10^{-6} bars. Valve 2 was closed and valve 4 was kept open. Helium was charged to volume V_I to greater

than 40 bars, by opening valves 1 and 8. After this, valves 1, 8, and 4 were closed. When the equilibrium was attained, pressure of the gas contained in volume V_a , was measured. Volume V_I was evacuated to a pressure of 5×10^{-6} bars and valve 2 was closed. The gas in volume V_a was expanded into V_I by opening valve 4 exactly one eighth turn. Pressure was measured after the attainment of equilibrium. Ratio V_I/V_a was determined using perfect gas relations because the pressure after expansion was approximately 0.14 bars.

Three sets of such readings were taken and the average value of V_I/V_a was used to apply the DPI correction.

CHAPTER V

EXPERIMENTAL RESULTS

A. Helium Calibration

The apparatus was calibrated with helium for isotherms at 298.15, 333.15, 353.15, 373.15, 393.15, and 413.15 K. Helium was selected as the calibration gas as it gives a linear pressure ratio versus pressure plot. This linear plot enables an accurate and precise determination of N , the importance of which has been discussed in Chapter I.

One run was made at each of the above temperatures and the pressures ranged from about 0.2 to 21 bars. In order to ensure thermal equilibrium, pressure readings were taken at the end of approximately three hours after each expansion. For an isotherm, large scale plots of the pressure ratio P_{r-1}/P_r versus the pressure P_{r-1} were drawn. For each isotherm this plot was linear and the intercept at $P_{r-1} = 0$ yielded the cell constant N , which could be read up to the fifth decimal place (Fig. 5). For temperatures other than 298.15 K, the actual value of N was determined by applying the DPI correction, as discussed in Chapter II. The corrected values of N are given in Table 1. As observed from Table 1, there is very little variation in the value of N with temperature. Hence, the average value

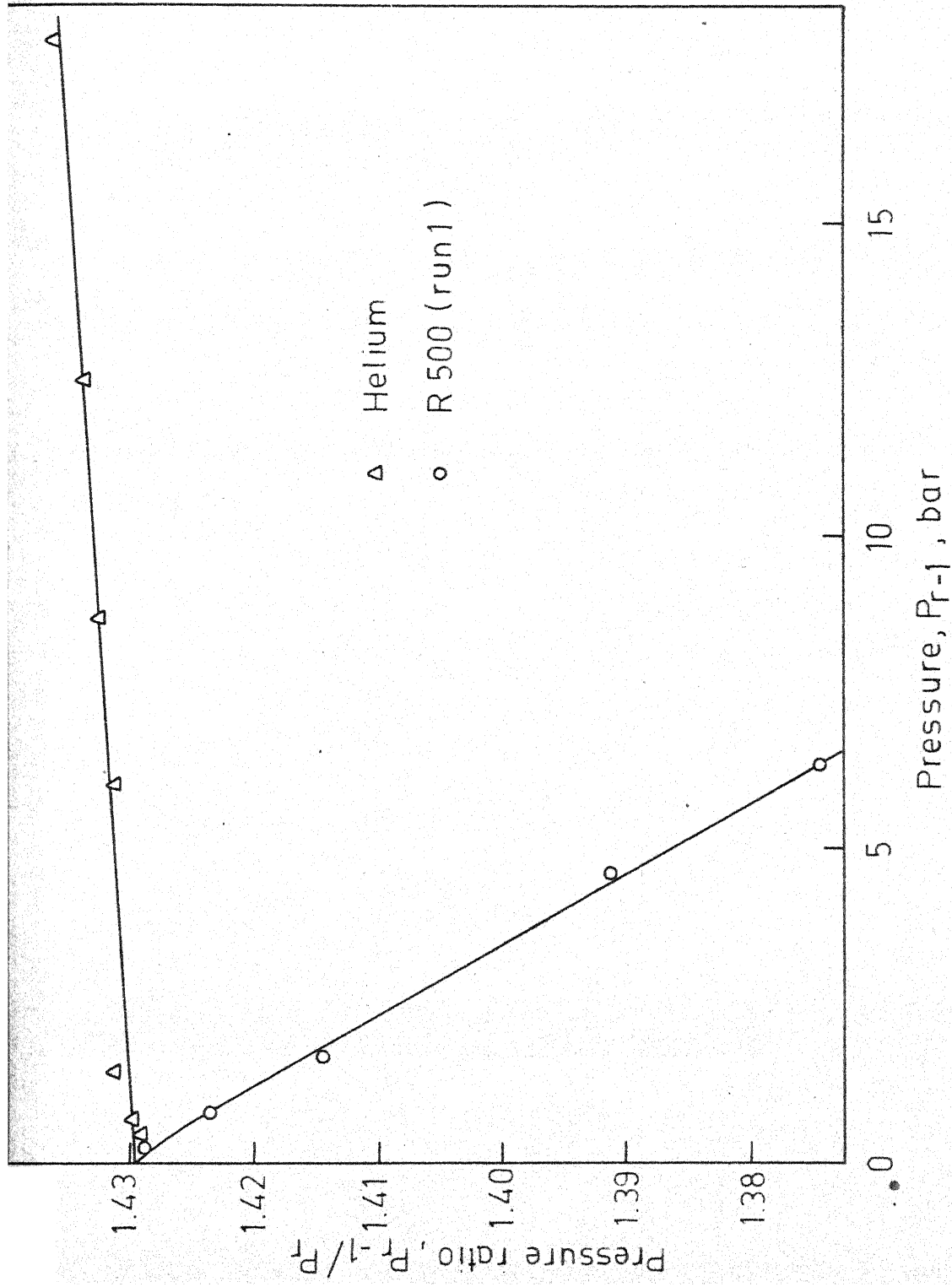


TABLE 1

Cell Constant, N, Using Helium

<u>Temperature, K</u>	<u>N</u>
298.15	1.42963
333.15	1.42966
353.15	1.42963
373.15	1.42958
393.15	1.42957
413.15	1.42954

Average value = 1.42961

of N was used in further calculations. The maximum probable error in this average value was estimated to be approximately 7 parts in 100,000.

The compression factors for helium were computed using Equation (12) and were smoothed by plotting the $(Z-1)/P$ versus P for each isotherm. The second virial coefficient at each isotherm was determined by extrapolating the linear plot of $(Z-1)/P$ versus P to zero pressure. The resulting second virial coefficients, B_p , are compared with the literature values in Table 2 and are plotted in Fig. 6.

The following values for V_I/V_a were obtained from three helium runs made for this purpose as described in Chapter IV.

Run	V_I/V_a
1	206.55079
2	206.55086
3	206.55078
Average value	206.55081

B. Refrigerant 500

Compression factor isotherms for R 500 vapour were measured at 298.15 K and from 313.15 to 413.15 K at 20 K interval for pressures upto 7 bars. The vapour pressure-boiling point data for R 500 is reported in Appendix H. At each temperature the maximum pressure was much lower than

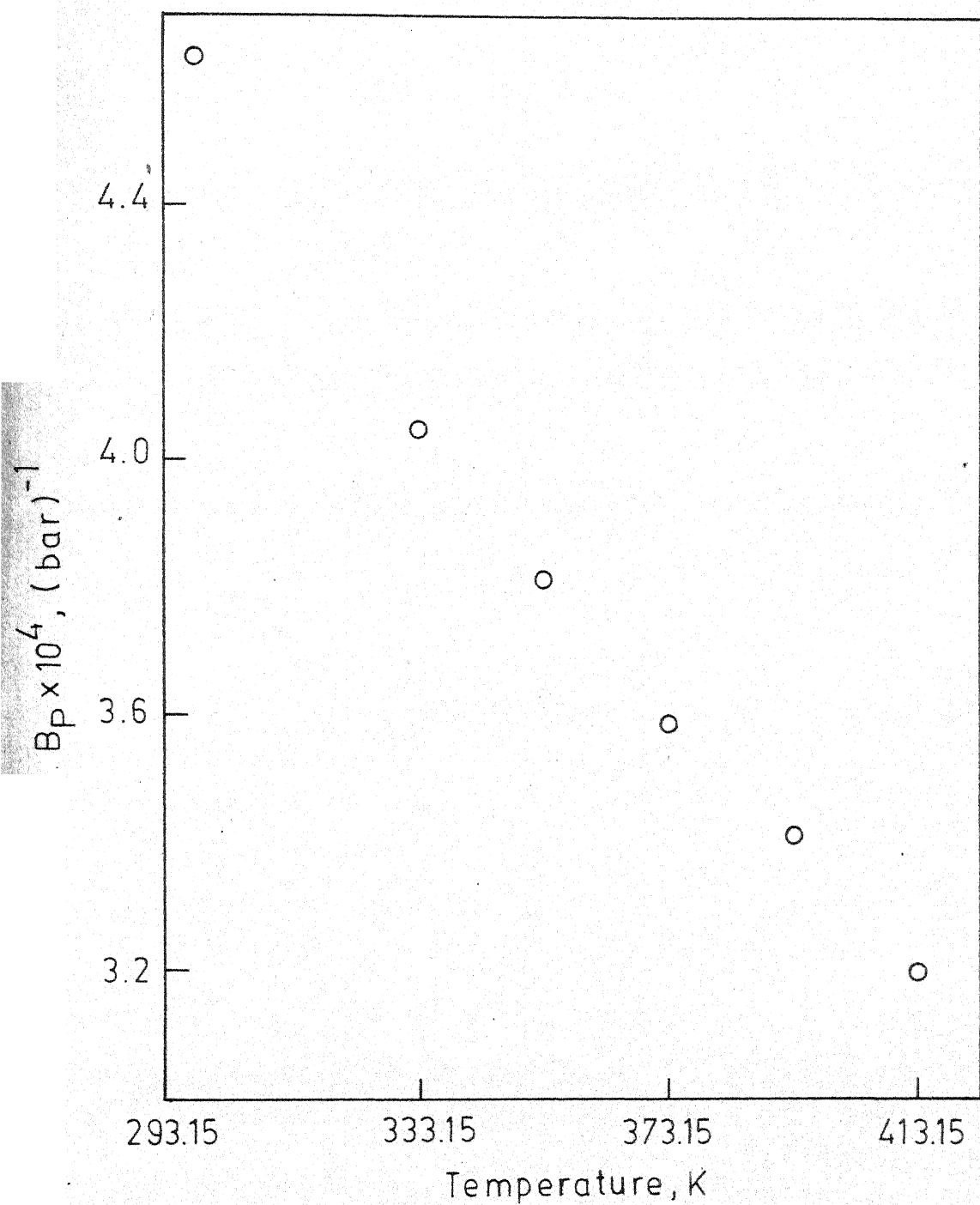


Fig. 6 - Second virial coefficients of helium.

the saturation pressure to ensure that the vapour was highly superheated. Three runs were made for each isotherm, except at 413.15 K in order to give evenly spaced data points. At 413.15 K, only two runs were made due to high rate of fuming of the bath oil at this temperature.

For each isotherm a plot of P_{r-1}/P_r versus P_{r-1} was made to determine the cell constant as suggested by Cox and Lawrenson (27). These plots had the usual negative slopes and extrapolation to zero pressure yielded values almost equal to that determined from the helium runs, differing only in the fourth decimal place. These plots for R 500 were not as linear as those obtained with helium. Also at lower pressures, the scatter with R 500 data was more as compared to the helium data. Hence the cell constant from the helium runs was used for all further computations with R 500 data. A sample plot of P_{r-1}/P_r versus P_{r-1} for the determination of cell constant, N , from the helium and R 500 runs at 298.15 K is shown in Fig. 5. For each run a plot of $P_r N^r$ versus P_r was made to determine the run constant (P_o/Z_o). The behaviour of this plot was very consistent for all the runs and it converged to a reasonable limiting value at zero pressure. The compression factors for R 500 were computed using Equation (12) and the DPI correction was applied as described in Chapter II. The experimental compression

factor data for R 500 are presented in Table 3. The following graphical procedure for smoothing the compression factors was followed.

1. A large scale plot of compression factor as a function of pressure was drawn for each isotherm. Smoothed curves were drawn through the experimental points.
2. A similar isobaric plot of compression factor as a function of temperature was made. The values of Z were interpolated from the Z - P plot. The Z values could be read to 1 part in 10,000 on all these plots.
3. In order to check whether the experimental compression factors were consistent with both pressure and temperature, the values of $(\partial Z/\partial P)_T$ and $(\partial Z/\partial T)_P$ were determined from the Z - P and the Z - T plots.
4. $(\partial Z/\partial P)_T$ values were plotted as a function of P and of T and, in turn, $(\partial Z/\partial T)_P$ values were plotted as a function of T and of P .
5. Smooth curves were drawn through these points, and the smoothed values of the slopes $(\partial Z/\partial P)_T$ and $(\partial Z/\partial T)_P$ were placed on the original Z - P and Z - T plots,
6. The original smoothed compression factor plots were then adjusted to match the smoothed slopes. Care was taken so that the final smoothed compression curves did pass

TABLE 3
Compression Factors of Refrigerant 500

Isotherm Temp., T K	Pressure, P bars	Z_{expt}	Z_{corr}
298.15	5.6963	0.9107	
	4.1287	0.9405	
	2.0953	0.9788	
	1.4823	0.9870	
	1.0481	0.9924	
	0.7286	0.9956	
	0.5120	0.9973	
	0.3577	0.9984	
298.15	6.1758	0.9015	
	4.4938	0.9335	
	3.2305	0.9574	
	1.6223	0.9852	
	1.1472	0.9912	
	0.7996	0.9950	
	0.5616	0.9970	
	0.3924	0.9981	
	0.2745	0.9988	
	0.1919	0.9992	

Isotherm K	Temp., T	Pressure, P bars	Z_{expt}	Z_{corr}
298.15		5.0457	0.9230	
		3.6397	0.9497	
		1.8431	0.9820	
		1.2977	0.9895	
		0.9063	0.9939	
		0.6361	0.9963	
		0.4469	0.9978	
		0.3130	0.9986	
		0.2180	0.9991	
		0.1518	0.9994	
313.15		7.3734	0.8986	0.8992
		5.3637	0.9320	0.9324
		3.8553	0.9565	0.9567
		1.9393	0.9856	0.9856
		1.3682	0.9920	0.9920
		0.9559	0.9955	0.9955
		0.6703	0.9973	0.9973
		0.4698	0.9983	0.9983
		0.3293	0.9990	0.9990

Isotherm K	Temp., T	Pressure, P bars	Z_{expt}	Z_{corr}
313.15		5.7350	0.9257	0.9262
		4.1314	0.9523	0.9525
		2.0825	0.9842	0.9842
		1.4705	0.9911	0.9911
		1.0431	0.9948	0.9948
		0.7213	0.9969	0.9969
		0.5060	0.9981	0.9981
		0.3542	0.9988	0.9988
313.15		6.4562	0.9138	0.9144
		4.6694	0.9433	0.9436
		3.3423	0.9653	0.9654
		1.6724	0.9890	0.9890
		1.1804	0.9937	0.9937
		0.8228	0.9963	0.9963
		0.5768	0.9978	0.9978
		0.4036	0.9987	0.9987
333.15		6.8825	0.9296	0.9303
		4.9519	0.9554	0.9558
		3.5328	0.9744	0.9747
		1.7612	0.9916	0.9918
		1.2402	0.9953	0.9953

Isotherm K	Temp., T	Pressure, P bars	Z_{expt}	Z_{corr}
333.15		0.8647	0.9973	0.9973
		0.6057	0.9984	0.9984
		0.4239	0.9990	0.9990
		0.2966	0.9993	0.9993
		6.1528	0.9395	0.9400
		4.4121	0.9635	0.9637
		3.1405	0.9793	0.9795
		1.5587	0.9932	0.9934
		1.0976	0.9961	0.9961
		0.7634	0.9977	0.9977
		0.5352	0.9986	0.9986
		5.5767	0.9471	0.9475
		3.9883	0.9684	0.9686
		1.9877	0.9900	0.9902
333.15		1.4003	0.9943	0.9943
		0.9765	0.9968	0.9968
		0.6852	0.9980	0.9980
		0.4796	0.9987	0.9987
		0.3356	0.9992	0.9992

Isotherm K	Temp., T	Pressure, P bars	Z_{expt}	Z_{corr}
353.15		6.9961	0.9432	0.9440
		5.0080	0.9643	0.9649
		3.5593	0.9796	0.9799
		1.7690	0.9937	0.9940
		1.2434	0.9965	0.9966
		0.8664	0.9978	0.9979
		0.606 6	0.9987	0.9987
		0.4245	0.9991	0.9991
353.15		6.3399	0.9501	0.9508
		4.5276	0.9692	0.9698
		3.2129	0.9832	0.9835
		1.5928	0.9949	0.9951
		1.1202	0.9969	0.9970
		0.7792	0.9982	0.9983
		0.5459	0.9988	0.9988
		0.3818	0.9992	0.9992
353.15		0.267 1	0.9994	0.9994
		5.6040	0.9580	0.9586
		3.9819	0.9751	0.9756
		1.9820	0.9925	0.9927
		1.3944	0.9958	0.9959
		0.9722	0.9974	0.9975

Isotherm k	Temp., T	Pressure, P Bars	Z_{expt}	Z_{corr}
373.15		0.681 4	0.9985	0.9985
		0.4773	0.9990	0.9990
		0.3345	0.9993	0.9993
		6.92 60	0.9541	0.9551
		4.935 1	0.9718	0.9725
		3.5000	0.9839	0.9844
		1.7311	0.9968	0.9970
		1.2172	0.9975	0.9976
		0.8469	0.9984	0.9985
		0.5940	0.9989	0.9989
		0.4148	0.9993	0.9993
		0.2903	0.9995	0.9995
373.15		6.1334	0.9607	0.9627
		4.3600	0.9764	0.9770
		3.0888	0.9875	0.9879
		1.5236	0.9966	0.9968
		1.0699	0.9980	0.9981
		0.7447	0.9986	0.9987
		0.5205	0.9991	0.9991
		0.3644	0.9994	0.9994

Isotherm K	Temp., T	Pressure, P Bars	Z_{expt}	Z_{corr}
373.15		5.5211	0.9664	0.9672
		3.9209	0.9803	0.9809
		1.9451	0.9961	0.9963
		1.3672	0.9970	0.9971
		0.9528	0.9983	0.9984
		0.6674	0.9988	0.9988
		0.4671	0.9992	0.9992
393.15		7.0811	0.9613	0.9623
		5.0307	0.9761	0.9766
		3.5596	0.9868	0.9870
		1.7581	0.9967	0.9968
		1.2350	0.9980	0.9981
		0.8596	0.9988	0.9988
		0.6016	0.9992	0.9992
		0.4209	0.9995	0.9995
393.15		6.2731	0.9671	0.9679
		4.4513	0.9802	0.9807
		3.1475	0.9898	0.9901
		1.5520	0.9974	0.9975
		1.0895	0.9983	0.9984
		0.7583	0.9989	0.9989
		0.5307	0.9993	0.9993

Isotherm K	Temp., T	Pressure, P Bars	Z _{expt}	Z _{corr}
393.15		5.6346	0.9717	0.9724
		3.9919	0.9837	0.9840
		1.9742	0.9960	0.9962
		1.3877	0.9978	0.9979
		0.9667	0.9985	0.9986
		0.6767	0.9991	0.9991
413.15		6.9022	0.9688	0.9700
		4.9834	0.9819	0.9822
		3.4560	0.9913	0.9914
		1.7030	0.9979	0.9980
		1.1952	0.9987	0.9988
		0.8322	0.9991	0.9992
		0.5817	0.9994	0.9994
		0.4073	0.9996	0.9996
413.15		5.7738	0.9760	0.9769
		4.0850	0.9870	0.9875
		2.0178	0.9970	0.9972
		1.4167	0.9984	0.9985
		0.9873	0.9989	0.9990
		0.6910	0.9992	0.9993
		0.4836	0.9995	0.9995

through the experimental points. In this way smoothed compression factors were obtained. The DPI correction was applied to these smoothed values and the corrected compression factors are also reported in Table 3 as Z_{corr} . The Z_{corr} versus P plot for each isotherm is shown in Fig. 7.

C. Error Analysis

Experimental errors in P , v , T data are comprised of random errors and systematic errors. However, the data should be relatively free of random errors due to a sufficiently large number of experimental points taken for each isotherm, use of high precision measurement devices, and the elaborate smoothing procedure discussed earlier in this Chapter. The systematic errors are due to the uncertainties in the measurements. Precision and accuracy of measurements are discussed below.

C.1. Temperature

The maximum uncertainty in the calibration of the platinum resistance thermometer was ± 0.0001 K. The thermometer bridge was capable of reading the resistance accurate to about ± 15 parts per million (ppm) or ± 0.00002 ohm, whichever is greater. Because of a relatively lower sensitivity of the DC galvanometer used to indicate the null condition, resistances could be read only to ± 0.001 ohm. The accuracy of the thermocouple calibration was therefore limited to ± 0.01 K.

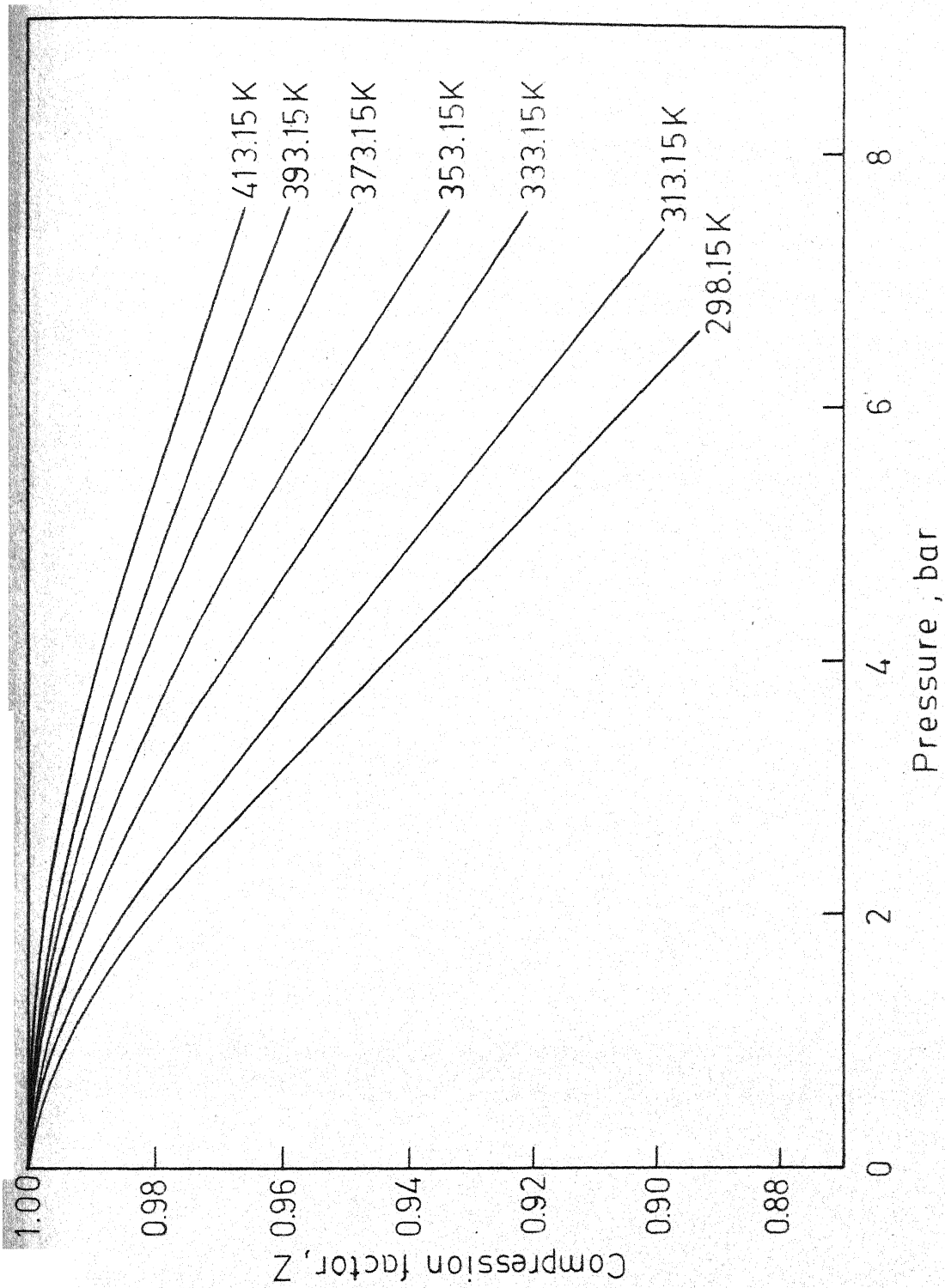


Fig. 7 - Compression factors of Refrigerant 500.

Type K-3 Universal potentiometer used to measure the thermocouple emf output, had an accuracy of ± 0.0001 mV. This corresponds to an accuracy of about ± 0.0031 K for chromel-constantan thermocouples employed in the present investigation. However, since the calibration of the thermocouples itself was not better than ± 0.01 K, the accuracy of temperature measurements was also limited to ± 0.01 K.

C.2. Pressure

Pressures were measured by the dead weight gauge (DWG) and the air piston gauge (APG). The masses used with the DWG were calibrated with a maximum uncertainty of 0.001 percent for 0.4536 Kg or above and a maximum uncertainty of 0.002 percent from 0.4536 to 0.04536 Kg. The uncertainty decreased to 0.998×10^{-6} Kg for masses below 0.04536 Kg. The piston area of the DWG was reported by the National Bureau of Standards to be accurate to 91 parts per million at 296.15 K. The maximum uncertainty in adding or removing masses on the DWG was $\pm 50 \times 10^{-6}$ Kg. The sensitivity of the DPIB and the DPIA was 13.8×10^{-6} bars/division. The error in determining the null point of the two DPIs was ± 2 scale divisions or a maximum uncertainty of 27.6×10^{-6} bars. The maximum uncertainty in measuring atmospheric pressure with the barometer was 6.8×10^{-7} bars. The APG was reported

to have an accuracy of 0.01 percent of reading or 6.9×10^{-6} bars whichever is greater.

The overall accuracy of pressure measurements depends upon the accuracy of the DWG and the APG. Hence, the measured pressures were estimated to be accurate to $\pm 10^{-4}$ bars.

C.3. Compression Factors

The effect of uncertainties in the pressure and temperature measurements on the compression factors may be estimated as follows.

$$dZ = \left(\frac{\partial Z}{\partial P}\right)_T dP + \left(\frac{\partial Z}{\partial T}\right)_P dT \quad (30)$$

If the accuracy of measurement is fairly good, Equation (30) may be replaced by,

$$\Delta Z = \left(\frac{\partial Z}{\partial P}\right)_T \Delta P + \left(\frac{\partial Z}{\partial T}\right)_P \Delta T \quad (31)$$

The highest values of the first derivatives were taken from the large scale plots made for the smoothing procedure.

Table 4 summarizes the sources of errors and the maximum total error in the compression factor for all temperatures. The individual errors have been estimated on the basis of their contribution to the compression factors.

TABLE 4

Summary of the Sources of Errors and the Maximum Total
Error in the Compression Factors

Source	Estimated Maximum Error (percent)
Pressure and Temperature Measurement	0.025
Evacuation	0.005
Cell Constant, N	0.03
(P_0/Z_0)	0.015
DPI Correction	0.01
Total	0.085

CHAPTER VI

QUANTITIES DERIVED FROM EXPERIMENTAL DATA

A. Virial Coefficients

Many empirical and semi-empirical relations have been used to describe the P , v , T relationships of gases and liquids. It is most convenient, however, and more satisfactory from the theoretical standpoint to use the Kammerlingh Onnes equation of state or any of the other simple variations of the virial equation,

$$Z = \frac{Pv}{RT} = 1 + \frac{B_v(T)}{v} + \frac{C_v(T)}{v^2} + \frac{D_v(T)}{v^3} + \frac{E_v(T)}{v^4} + \dots \quad (32)$$

$$Z = \frac{Pv}{RT} = 1 + B_p(T)P + C_p(T)P^2 + D_p(T)P^3 + E_p(T)P^4 + \dots \quad (33)$$

Equation (32) is referred to as the Leiden virial expansion and Equation (33) as the Berlin virial expansion. The virial coefficients B_v , C_v , D_v , E_v , ... and B_p , C_p , D_p , E_p , ... are temperature dependent and are expressed in units of powers of volume or reciprocal pressure, depending upon the form of equation used. The Berlin expansion is mathematically equivalent to Lieden expansion and the coefficients of the two expansions are uniquely related to each other. The

first few relations are (1),

$$B_V = B_P RT \quad (34)$$

$$C_V = (C_P + B_P^2) (RT)^2 \quad (35)$$

$$D_V = (D_P + 3C_P B_P + B_P^3) (RT)^3 \quad (36)$$

$$E_V = (E_P + 4D_P B_P + 6C_P B_P^2 + 2C_P^2 + B_P^4) (RT)^4 \quad (37)$$

$$D_P = B_V / RT \quad (38)$$

$$C_P = (C_V - B_V^2) / (RT)^2 \quad (39)$$

$$D_P = \frac{D_V - 3B_V C_V + 2B_V^3}{(RT)^3} \quad (40)$$

$$E_P = \frac{E_V - 2C_V^2 - 4B_V D_V + 10B_V^2 C_V - 5B_V^4}{(RT)^4} \quad (41)$$

In the present investigation, it was convenient to use the Berlin expansion in order to determine the virial coefficients because of the form of the experimental data. The virial coefficients B_P , C_P , D_P , ... were calculated graphically by rearranging Equation (33), truncated upto the fifth virial coefficient, as follows:

$$\frac{Z-1}{P} = B_P + C_P P + D_P P^2 + E_P P^3 \quad (42)$$

$$\lim_{P \rightarrow 0} \left(\frac{Z-1}{P} \right) = B_P \quad (43)$$

$$\frac{\left(\frac{Z-1}{P} \right) - B_P}{P} = C_P + D_P P + E_P P^2 \quad (44)$$

$$\lim_{P \rightarrow 0} \frac{\left(\frac{Z-1}{P} \right) - B_P}{P} = C_P \quad (45)$$

$$\frac{\frac{\left(\frac{Z-1}{P} \right) - B_P}{P} - C_P}{P} = D_P + E_P P \quad (46)$$

$$\lim_{P \rightarrow 0} \frac{\frac{\left(\frac{Z-1}{P} \right) - B_P}{P} - C_P}{P} = D_P \quad (47)$$

The corrected experimental compression factors reported in Table 3 and Equations (43), (45), and (47) were used in succession to calculate B_P , C_P , and D_P for R 500 and are reported in Table 5. The second virial coefficient as a function of temperature is shown in Fig. 8.

B. Thermodynamic Properties

The thermodynamic properties of a real gas can be taken as the sum of the quantity for the perfect gas and a

TABLE 5

Second, Third, and Fourth Virial Coefficients
of Refrigerant 500

T, K	$-B_P \times 10^4, (\text{bar})^{-1}$	$-C_P \times 10^4, (\text{bar})^{-2}$	$D_P \times 10^4, (\text{bar})^{-3}$
298.15	38.75	30.16	1.59
313.15	30.61	23.42	1.23
333.15	23.86	16.43	0.75
353.15	19.17	11.23	0.36
373.15	15.50	8.53	0.21
393.15	12.24	6.86	-
413.15	9.40	5.20	-

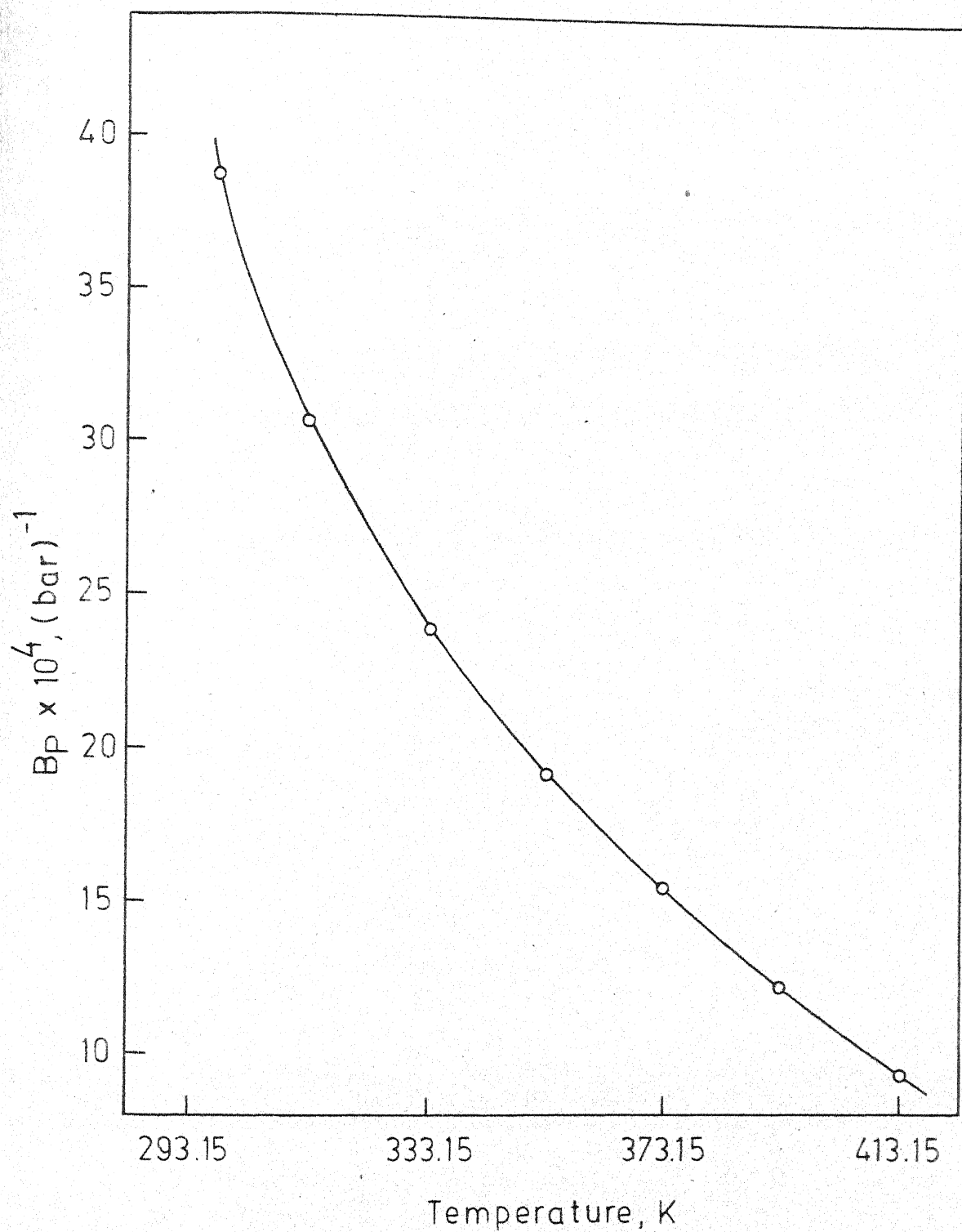


Fig. 8 - Second virial coefficients of Refrigerant 500.

term giving the effect of gas imperfection. The corrections for the gas imperfection are generally called departure functions and are determined primarily from the experimental P, v, T measurements. For example, $(H - H^0)$ is the enthalpy of the gas in the real gas state less that of the gas in the standard state at the same temperature. For a gaseous substance, the standard state is the ideal gaseous state at unit pressure (in bars) at each temperature. At a given temperature the standard state is a constant. The thermodynamic properties H^0 , C_p^0 , etc., are for the gas in the standard state, which is the ideal gas at one bar pressure.

Enthalpy Content $(H - H^0)_T$

From the definitions of enthalpy and entropy and from the Maxwell relations (62), we obtain

$$\left(\frac{\partial H}{\partial P}\right)_T = v - T \left(\frac{\partial v}{\partial T}\right)_P \quad (48)$$

Since any gas approaches the perfect gas state as zero pressure is approached, integration of Equation (48) at constant temperature from zero to final pressure P yields $(H - H^0)_T$

$$(H - H^0)_T = \int_0^P \left(\frac{\partial H}{\partial P}\right)_T dP = \int_0^P \left[v - T \left(\frac{\partial v}{\partial T}\right)_P \right] dP \quad (49)$$

Substituting the virial equation, i.e., Equation (33) truncated after the fourth virial coefficient, into Equation (49) yields after integration,

$$(H - H^0)_T = -RT^2 \left[\left(-\frac{dB_P}{dT} \right) P + \left(-\frac{dC_P}{dT} \right) \frac{P^2}{2} + \left(-\frac{dD_P}{dT} \right) \frac{P^3}{3} \right] \quad (50)$$

Entropy Content $(S - S^0)_T$

The change in entropy with pressure is given by,

$$\left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial v}{\partial T} \right)_P \quad (51)$$

Because the entropy of a gas is infinite at zero pressure, the standard state is defined as the hypothetical ideal gas at 1 bar pressure. Since $(\partial v / \partial T)_P$ for a perfect gas is R/P , we have

$$\begin{aligned} (S - S^0)_T &= - \int_0^P \left(\frac{\partial v}{\partial T} \right)_P dP + \int_0^{1 \text{ bar}} \frac{R}{P} dP \\ &= \int_0^P \left[\frac{R}{P} - \left(\frac{\partial v}{\partial T} \right)_P \right] dP - R \ln P \end{aligned} \quad (52)$$

Substituting from Equation (33) and integrating the resulting expression, we obtain,

$$\begin{aligned} (S - S^0)_T &= -R \left[B_P P + C_P \frac{P^2}{2} + D_P \frac{P^3}{3} \right] \\ &\quad - RT \left[\left(-\frac{dB_P}{dT} \right) P + \left(-\frac{dC_P}{dT} \right) \frac{P^2}{2} + \left(-\frac{dD_P}{dT} \right) \frac{P^3}{3} \right] \\ &\quad - R \ln P \end{aligned} \quad (53)$$

Gibbs Energy Content $(G - G^0)_T$

At constant temperature and for pressure P , we have (62),

$$(G - G^0)_T = - \int_0^P \left[\frac{RT}{P} - v \right] dP + RT \ln P \quad (54)$$

Substitution of Equation (33) into Equation (54) yields after integration,

$$(G - G^0)_T = RT \left[B_P P + C_P \frac{P^2}{2} + D_P \frac{P^3}{3} \right] + RT \ln P \quad (55)$$

The respective thermodynamic properties as a function of pressure at each temperature were calculated from Equations (50), (53), and (55). The necessary slopes were obtained from the large scale plots of the virial coefficients versus temperature. The calculated thermodynamic properties are reported in Table 6. The ideal gas thermodynamic properties with formulas to calculate them are given in Appendix I (63).

C. Fugacity Coefficients

The differential relationship between fugacity and pressure is,

$$\left(\frac{\partial \ln f}{\partial P} \right)_T = \frac{v}{RT} \quad (56)$$

Rearranging Equation (56), we have

TABLE 6

THERMODYNAMIC PROPERTIES OF REFRIGERANT 500

T, K	P, bars	$-(H-H^0)_T$ J mole ⁻¹	$-(S-S^0)_T$ JK ⁻¹ mole ⁻¹	$(G-G^0)_T$ J mole ⁻¹	$\gamma = f/P$
298.15	0.2	9.7	-13.4	-3991.8	0.9992
	0.5	27.0	- 5.7	-1724.0	0.9977
	1.0	62.6	0.2	- 13.2	0.9947
	1.5	106.4	3.7	982.7	0.9910
	2.0	157.9	6.2	1685.2	0.9867
	3.0	282.3	9.8	2664.5	0.9765
	4.0	432.2	12.7	3346.7	0.9644
	5.0	604.2	15.0	3864.6	0.9508
	6.0	794.7	17.0	4277.8	0.9360
	7.0	1000.1	18.8	4618.4	0.9205
	8.0	1216.8	20.5	4906.0	0.9045
313.15	0.2	7.8	-13.4	-4192.1	0.9993
	0.5	21.8	- 5.7	-1809.5	0.9982
	1.0	51.1	0.1	- 10.9	0.9958
	1.5	87.4	3.6	1037.2	0.9929
	2.0	130.1	6.1	1777.4	0.9896
	3.0	233.1	9.7	2811.9	0.9816
	4.0	356.1	12.4	3535.6	0.9720

T, K	P, bars	$-(H-H^O)_T$ J mole ⁻¹	$-(S-S^O)_T$ JK ⁻¹ mole ⁻¹	$(G-G^O)_T$ J mole ⁻¹	$\gamma=f/P$
	5.0	495.3	14.6	4087.7	0.9613
	6.0	646.7	16.5	4530.6	0.9496
	7.0	806.4	18.2	4897.9	0.9373
	8.0	970.6	19.7	5209.9	0.9246
333.15	0.2	6.1	-13.4	-4459.5	0.9995
	0.5	17.3	- 5.7	-1923.8	0.9986
	1.0	41.2	0.1	- 8.8	0.9968
	1.5	71.2	3.5	1108.3	0.9947
	2.0	106.7	6.0	1898.2	0.9922
	3.0	191.6	9.6	3004.7	0.9862
	4.0	292.3	12.2	3781.5	0.9791
	5.0	403.7	14.3	4376.8	0.9711
	6.0	521.6	16.1	4856.5	0.9622
	7.0	641.4	17.7	5256.1	0.9528
	8.0	758.9	19.1	5596.9	0.9428
353.15	0.2	4.5	-13.4	-4726.9	0.9989
	0.5	12.8	- 5.7	-2038.5	0.9996
	1.0	30.6	0.1	- 7.2	0.9975
	1.5	53.3	3.5	1178.5	0.9959
	2.0	80.9	5.9	2017.7	0.9940

T, K	P, bars	$-(H-H^{\circ})_T$ J mole ⁻¹	$-(S-S^{\circ})_T$ JK ⁻¹ mole ⁻¹	$(G-G^{\circ})_T$ J mole ⁻¹	$\gamma = f/P$
	3.0	150.9	9.5	3195.0	0.9896
	4.0	240.6	12.1	4023.8	0.9842
	5.0	350.0	14.2	4660.7	0.9781
	6.0	479.1	16.0	5175.5	0.9713
	7.0	627.9	17.7	5605.5	0.9639
	8.0	796.4	19.2	5973.2	0.9559
373.15	0.2	4.0	-13.4	-4994.3	0.9997
	0.5	18.9	- 5.7	-2153.2	0.9991
	1.0	24.9	0.1	- 6.1	0.9980
	1.5	42.1	3.5	1247.8	0.9967
	2.0	62.5	5.9	2135.8	0.9953
	3.0	112.9	9.4	3382.9	0.9917
	4.0	176.0	11.8	4262.0	0.9875
	5.0	251.8	13.9	4938.9	0.9826
	6.0	340.4	15.6	5487.2	0.9771
	7.0	441.7	17.1	5946.2	0.9711
	8.0	555.7	18.5	6339.5	0.9645

T, K	P, bars	$-(H-H^0)_T$ Jmole ⁻¹	$-(S-S^0)_T$ JK ⁻¹ mole ⁻¹	$(G-G^0)_T$ Jmole ⁻¹	$\gamma = f/P$
393.15	0.2	4.1	-13.4	-5261.8	0.9997
	0.5	11.1	- 5.7	-2268.0	0.9993
	1.0	25.1	- 0.1	- 5.1	0.9984
	1.5	41.9	3.5	1316.9	0.9974
	2.0	61.7	5.9	2253.3	0.9962
	3.0	109.9	9.4	3569.1	0.9933
	4.0	169.6	11.9	4497.6	0.9897
	5.0	241.0	13.9	5212.9	0.9854
	6.0	323.9	15.6	5792.6	0.9805
	7.0	418.3	17.0	6277.9	0.9749
	8.0	524.3	18.4	6693.5	0.9688
413.15	0.2	4.4	-13.4	-5529.2	0.9998
	0.5	11.8	- 5.7	-2382.8	0.9995
	1.0	26.0	0.1	- 4.1	0.9988
	1.5	42.6	3.5	1386.0	0.9980
	2.0	61.6	5.9	2373.0	0.9971
	3.0	107.2	9.4	3756.1	0.9949
	4.0	162.4	11.9	4734.8	0.9931
	5.0	227.5	13.8	5490.1	0.9889
	6.0	302.3	15.5	6103.3	0.9851
	7.0	387.0	17.0	6618.0	0.9809
	8.0	481.4	18.3	7060.1	0.9761

$$\frac{\partial \ln (f/P)}{\partial P} = \frac{\partial \ln f}{\partial P} - \frac{\ln P}{P} = \frac{V}{RT} - \frac{1}{P} \quad (57)$$

Integrating Equation (57) from a low pressure P_1 to the final pressure P_2 yields,

$$\ln \frac{f_2}{P_2} - \ln \frac{f_1}{P_1} = \int_{P_1}^{P_2} \left(\frac{V}{RT} - \frac{1}{P} \right) dP \quad (58)$$

However, the fugacity is equal to the pressure at zero pressure; hence,

$$\ln \frac{f}{P} = \int_0^P \left(\frac{V}{RT} - \frac{1}{P} \right) dP \quad (59)$$

Substituting from Equation (33), we obtain,

$$\ln \frac{f}{P} = \int_0^P \left[B_P + C_P P + D_P P^2 \right] dP \quad (60)$$

$$\ln \frac{f}{P} = B_P P + C_P \frac{P^2}{2} + D_P \frac{P^3}{3} \quad (61)$$

The fugacity coefficient γ is defined as,

$$\gamma = \frac{f}{P} \quad (62)$$

The relationship between fugacity and Gibbs energy is,

$$(G - G^0)_T = RT \ln f \quad (63)$$

The fugacity coefficients calculated from Equation (61) are reported in Table 6.

CHAPTER VII

DISCUSSION OF RESULTS

A. Helium

The second virial coefficients of helium obtained in the present investigation agree very well with the reliable published values as shown in Table 2. This confirms the reliability of the apparatus fabricated and used in the present investigation.

B. Refrigerant 500

B.1 Compression Factors

This is the first time that the low pressure compression factors have been reported for Refrigerant 500 from 298.15 to 413.15 K. The lowest pressures investigated by Sinka and Murphy (12) are of the order of 14 bars at about 330 K. Any attempt for comparison of our results with their data requires considerable extrapolation. It is therefore not possible to compare the present results with the published literature. The compression factor versus pressure plot displayed in Fig. 7 shows the expected behaviour. For any isotherm, as pressure approaches zero, Z tends to unity in accordance with the definition of the perfect gas.

In the present investigation, it has been possible to go to pressures as low as 0.2 bars which is the salient feature of this work. The lack of a high temperature DPI and the fact that the DWG and the APG do not overlap in their pressure ranges are the two factors which limit the capability of the apparatus. The former requires a correction to be applied to compression factors, the DPI correction, whereas, the latter forces us to skip the pressure falling in the range 2 to 3 bars. Experimental pressure could not be measured for one expansion at each temperature. This posed a problem in the DPI correction which uses the pressure and the compression factor sequences. In the application of the DPI correction [Equations (26), (28), (29)], ϕ values are involved. For example, calculation of Z_4 at P_4 involves the use of Z_3 and Z_{3a} at P_3 . If P_3 is skipped, one has to go to P_2 and get a relation for Z_4 in terms of P_2 and not P_3 . This expression contains ϕ_3 at P_3 which is not known. In this situation ϕ_2 was used for ϕ_3 . This introduced an uncertainty in the calculated compression factors beyond the skipped pressure. The total uncertainty due to the DPI correction was therefore estimated to be 0.01 percent.

The total uncertainty in the compression factors is lower than 0.1% as reported in Table 4. With the use of

a high temperature DPI and the proper pistons for the gauges, the uncertainty can be brought down to about 0.05%. Further attempts should be in this direction.

B.2 Virial Coefficients

It is expected that because of the very low pressures involved in present work, reliable second virial coefficients have been obtained for R 500. The third virial coefficients are found to be relatively large for R 500 at temperatures upto 373 K and indicate substantial ternary interactions under these conditions. The fourth virial coefficients reported in Table 5 have very little significance because of the scatter in data at low pressures.

An attempt was made to compute the second virial coefficients from the data of Sinka and Murphy (12), but it involved considerable interpolation and extrapolation and meaningful values could not be derived.

B.3 Thermodynamic Properties

The departure functions are reported in Table 6 for R 500 from 0.2 to 8 bars pressure at each isotherm. The ideal gas thermodynamic properties required to obtain the R 500 real gas properties have been computed from R 12 and R 152a data (63,64) using the mixing rules. Morsy (13) used the data of Sinka and Murphy to compute thermodynamic

properties of R 500. Unfortunately, these data were not available for comparison. The departure functions are estimated to be accurate to about 1 to 2%.

CHAPTER VIII

SUMMARY AND CONCLUSIONS

A Burnett-type apparatus was fabricated to measure accurate P, v, T data. Pressures could be measured accurately to $\pm 10^{-4}$ bars with the help of DWG and APG. Temperatures were measured accurate to ± 0.01 K with thermocouples calibrated against a platinum resistance thermometer. The range of temperature of investigation was limited from 298.15 to 413.15 K due to the quality of the bath oil. Silicone oil could not be used because of very high costs.

The apparatus was checked with helium satisfactorily as shown by the comparison of its second virial coefficients with reliable literature values. The P, v, T data for Refrigerant 500 were obtained from 298.15 to 413.15 K and the pressures ranged from about 0.2 to 7 bars for each isotherm. Such low pressure data are reported for the first time and should prove useful in extending the range of the available P, v, T data. The P, v, T data for R 500 are now available from 298.15 to 480 K and for pressures 0.2 to 60 bars.

The second and the third virial coefficient data should throw some light on the intermolecular forces. The real gas thermodynamic properties at low pressures should prove useful to the design engineers for the design of refrigeration and other systems.

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APPENDIX A

THERMOCOUPLE CALIBRATION DATA

$\frac{R_t}{\text{Ohms}}$	$\frac{T}{K}$	Thermocouples, (mV)			
		1	2	3	4
27.174	308.57145	2.1275	2.1375	2.1370	2.1224
30.614	322.87456	3.0389	3.0383	3.0225	3.0216
31.690	333.60227	3.7229	3.7174	3.7135	3.7172
32.629	342.99223	4.3294	4.3263	4.3172	4.3167
33.974	356.48852	5.2175	5.2142	5.2136	5.201
35.385	370.70650	6.1726	6.1609	6.1568	6.1601
36.77	384.72242	7.1254	7.1219	7.1099	7.1193

APPENDIX B

REPORT OF CALIBRATION

DEAD-WEIGHT GAUGE AND WEIGHTS

TEST REPORT
DEAD-WEIGHT GAUGE

Type: 2400 Serial No. 16921 Date: 12.12.69

Submitted by: EDUCATION DEVELOPMENT CENTRE P.O. K-6913
 KANPUR INDO-AMERICAN PROGRAM

Manufacturer: RUSKA Job No. A-9987/C-981

INSTRUMENT CONSTANTS

Piston and Cylinder

Assembly Number HCR-41

Range 30 to 12000 psi

A_0 at 23°C 0.0260389 in^2

$b(\text{in}^2/\text{in}^2)$ $-1.8 \times 10^{-8}/\text{psi}$

Thermal Coefficient (in^2/in^2) $9.1 \times 10^{-6}/^\circ\text{C}$

Piston Material Tungsten Carbide

Cylinder Material Tungsten Carbide

Plane of Reference (Distance below
Top Loading Edge of Weight Table) 7.96 in

Tare Components (Pound)	Apparent Mass	True Mass
Piston Assembly	0.057430	
Weight Loading Table	0.723657	
Other	0.0	
Surface Tension*	0.000150	
Total	0.781237	

Fluid used in this test Spinesstic No.38

Observed Sink Rate (5000 PSI) 0.02 in/min (maximum) at 25.5°C

* Estimated total effects of surface tension and of lubricating oil on the weight table spindle.

This calibration was made by intercomparing the above Dead Weight Gauge with Ruska Instrument Corporation Laboratory Gauge Piston No. AS-7(S4). This piston is referenced to National Bureau of Standards Test Number 167720 and 174192, which was issued for the standard piston at Ruska Instrument Corporation.

The systematic error in the reported value of A_0 is estimated to be 91 parts per million. The standard deviation of the random errors of 5 independent observations in the comparison is 2.7 PPM. The uncertainty in the reported value of b is estimated to be $\pm 2.7 \times 10^{-9}$ /psi. The reported value of mass for the sum of the tare components is estimated to be correct within 20 PPM and is referenced to NBS Test Number 198182.

Date: 12.12.69

Vice President-Technical Services
RUSKA INSTRUMENT CORPORATION

TEST REPORT

PRESSURE GAUGE WEIGHTS

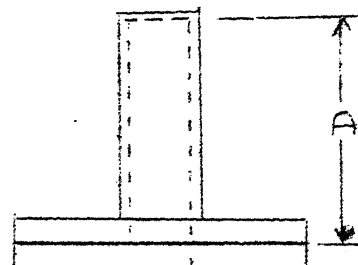
Type: 2402

Serial No. 16925

Date: 12.23.69

Material: 303 ST ST Density: 7.8 g cm^{-3} Submitted by: EDUCATION DEVELOPMENT CENTRE
KANPUR INDO-AMERICAN PROGRAM

Manufacturer: RUSKA Job: A9995/C-9816

Depth of locating
seat from line on
weight A; $D=7.94 \text{ in}$ Denomination
Approximate Pressure (PSI)
Piston Area: 0.026 in^2 Apparent Mass vs.
Brass Standards
(M_A Pounds)

Designation

1000	26.03549	A
1000	26.03595	B
1000	26.03604	C
1000	26.03613	D
1000	26.03609	E
1000	26.03607	F
1000	26.03600	G
1000	26.03598	H
1000	26.03579	I
1000	26.03563	J
1000	26.03585	K
500	13.01844	L
200	5.20721	M
200	5.20713	N
100	2.60362	O
50	1.30180	P
20	0.520734	Q
20	0.520734	R
10	0.260377	S
5	0.130203	T
2	0.052071	U
2	0.052087	V
1	0.026051	W
0.5	0.013025	X

STATEMENT OF ACCURACY
MASSES FOR DEAD WEIGHT GAUGE

The values of mass listed in this report were derived from Ruska Instrument Corporation master weights which were calibrated by the National Bureau of Standards under Test No. 2.6/167716, Set A and Set B, and 198182.

Deviation from the true value of mass will not exceed the following limits:

<u>Range</u> Pounds	<u>Deviation</u>
to 0.1	2.2×10^{-6} Pounds
0.1 to 1.0	0.002%
1.0 up	0.001%

Reference: Serial No. 16925

Ruska Job No. A9995/C-9816

Date: December 23, 1969

Vice President-Technical Services

RUSKA INSTRUMENT CORPORATION

APPENDIX C

REPORT OF CALIBRATION

AIR PISTON GAUGE AND WEIGHTS

TEST REPORT
DEAD-WEIGHT GAUGE

Type: 2465-751-00 Serial No. 17360 Date: June 19, 1979
 Submitted by: INDIA SUPPLY MISSION P.O. J/H-3353/AID-164/D/V/
 Manufacturer: RUSKA Job No. A-0603/C-0268
 8354

INSTRUMENT CONSTANTS

Piston and Cylinder
 Assembly Number L-241
 Range 0.2 to 15 psi
 A_0 at 23°C 0.520302 in²
 b (in²/in²) 0.0/psi
 Thermal Coefficient (in²/in²) $2.0 \times 10^{-5}/^{\circ}\text{C}$
 Piston Material 440 C Stainless Steel
 Cylinder Material 440 C Stainless Steel
 Plane of Reference (Distance below
 Top Loading Edge of Weight Table) 1.6 in

Tare Components (Pound)	Apparent Mass	True Mass
Piston Assembly	0.104053	0.104054
Weight Loading Table	0.0	0.0
Other	0.0	0.0
Surface Tension*	0.0	0.0
Total	0.104053	0.104054
Fluid used in this test	Nitrogen Gas	
Observed Sink Rate (15 PSI)	0.05 in/min (maximum) at 25°C	

* Estimated total effects of surface tension and of lubricating oil on the weight table spindle.

This calibration was made by intercomparing the above Dead Weight Gauge with Ruska Instrument Corporation Laboratory Gauge Piston No. L-54. This piston is referenced to National Bureau of Standards Test Number F7195/TN 194533, which was issued for the standard piston at Ruska Instrument Corporation.

The systematic error in the reported value of A_0 is estimated to be 65 parts per million. The standard deviation of the random errors of 6 independent observations in the comparison is 2.0 PPM. The reported value of mass for the sum of the tare components is estimated to be correct within 20 PPM and is referenced to NBS Test Number 198132.

Date: June 19, 1970

Vice President-Technical Services
RUSKA INSTRUMENT CORPORATION

TEST REPORT
PRESSURE GAUGE WEIGHTS

Purchaser: INDIA SUPPLY MISSION Test Completed: June 23, 1970
Catalog No. 2465-780-00 Serial No.: 17383
Manufacturer: RUSKA Job No.: A-0581/C-0268

Designation	Denomination PSI	Density	Apparent Mass vs. Brass Standards	True Mass
	0.520 in ² Piston	g cm ⁻³	Pounds	Pounds
A	2.5	7.8	1.30080	1.30081
B	2.5	7.8	1.30080	1.30081
C	2.5	7.8	1.30073	1.30074
D	2.5	7.8	1.30076	1.30077
E	2.5	7.8	1.30075	1.30076
G	1.0	7.8	0.520313	0.520319
H	1.0	7.8	0.520315	0.520321
I	0.5	7.8	0.260142	0.260145
J	0.25	7.8	0.130074	0.130075
K	0.1	7.8	0.0520346	0.0520352
L	0.1	7.8	0.0520326	0.0520332
M	0.05	7.8	0.0260209	0.0260212
N	0.025	7.8	0.0130130	0.0130131
O	0.0125	7.8	0.0065034	0.0065035

STATEMENT OF ACCURACY
MASSES FOR DEAD-WEIGHT TESTER

The values of mass listed in this report were derived from Ruska Instrument Corporation master weights, which were calibrated by the National Bureau of Standards under Test No. 2.6/167716, Set A and Set B, and 193132.

Deviation from the true value of mass will not exceed 10 PPM or 0.0001 g, whichever is greater.

Reference: Serial No. 17383

Ruska Job No. A-0581/C-0268

Date: June 23, 1970

Vice President-Technical Services
RUSKA INSTRUMENT CORPORATION

APPENDIX D

CALIBRATION OF FRACTIONAL
STAINLESS STEEL WEIGHTS

Designation	Apparent Mass vs. Brass standards
-----	----- grams
20 gm	19.99512
10 gm	9.99400
5 gm	4.99019
2 gm	1.99595
2* gm	1.99578
1 gm	1.00000
500 mg	0.50000
200 mg	0.22323
200*mg	0.20013
200**mg	0.21619
100 mg	0.09500
50 mg	0.04829

APPENDIX E

EXPERIMENTAL PRESSURE AND TEMPERATURE DATA FOR HELIUM

CALIBRATION

Ex- pan- sion	DWG/APG weights Designation	Gauge Temp. K	Barometric pressure Meter of mercury	Barometric temperature K	Corrected pressure Bars
T = 298.15 K					
0	100mg+200mg +500mg+X+S+N +TARE+50mg/2	293.15	0.7509	297.04	17.5698
1	500mg+5gm+X+U +S+Q+O+TARE	293.55	0.7532	296.76	12.2333
2	200*mg+200mg +2gm+U+V+T +Q+P+TARE	295.55	0.75245	297.04	18.5331
3	200mg+500mg +1gm+2gm+X+W +Q+R+TARE	295.55	0.7506	297.04	5.9580
4	200mg+500mg +2gm+X+T+S* +TARE+200*mg/2	295.65	0.7504	297.66	4.1636
5					
6	500mg+2gm+N+K +H+G+E+D+C+B +A+TARE	295.95	0.7509	297.04	2.0244

TARE denotes total mass of the tare components of piston gauge assembly.

Ex- pan- sion	DWG/APG weights Designation	Gauge Temp. K	Barometric pressure Meter of mercury	Barometric temperature K	Corrected pressure Bars
7	2gm+O+N+L+K+I +B+A+TARE	296.75	0.75135	297.04	1.4133
8 ^a	M+I+G+E+D+C+B +A+TARE	295.35	0.7514	297.04	0.9814
9	O+J+H+G+C+B+A +TARE	296.15	0.7527	298.15	0.6863
10	N+J+I+G+B+A +TARE	297.05	0.75115	298.43	0.4807
T = 333.15 K					
0	200mg+500mg +1gm+2gm+2*gm +W+T+S+Q+N +TARE	296.25	0.7508	297.87	19.3525
1	200mg+2gm+W+P +O+TARE	294.85	0.75095	298.43	13.4840
2	200mg+500mg +5gm+X+W+Q+R+P +TARE+200*mg/2	295.15	0.7500	297.04	9.4097

a denotes that pressure has fallen below one atmosphere from expansion no. 8 and onwards and has been measured with reference to a pressure of 6.8×10^{-4} bars.

Ex- pan- sion	DWG/APG weights Designation	Gauge Temp. K	Barometric pressure Meter of mercury	Barometric temperature K	Corrected pressure Bars
3	200mg+200*mg +200**mg+2gm +X+P+TARE	296.05	0.7493	297.59	6.56915
4	200mg+500mg+5gm +X+W+R+TARE +100mg/2	296.35	0.74915	297.87	4.5919
5	200mg+200*mg +500mg+2gm +2*gm+X+W+TARE	296.55	0.74925	297.87	3.2110
6					
7	O+N+M+J+B+A +TARE	295.15	0.7493	297.32	1.5545
8	K+G+TARE	295.25	0.74945	297.32	1.0911
9 ^a	N+K+J+I+D+C +B+A+TARE	296.65	0.7499	298.43	0.7629
10	C+B+A+TARE	296.85	0.7499	298.43	0.5306
T = 353.15 K					
O	200mg+1gm+2gm +X+W+V+T+S+Q+P +O+TARE+200*mg/2	299.25	0.7470	299.82	16.0655

Ex- pan- sion	DWG/APG weights Designation	Gauge Temp. K	Barometric pressure Meter of mercury	Barometric temp. K	Corrected pressure Bars
1	100mg+500mg+1gm +W+V+T+S+O+ +TARE+200mg/2	298.85	0.7469	299.82	11.2052
2	100mg+200mg +500mg+5gm+X+W +V+T+S+P+TARE	296.85	0.7474	298.71	7.8239
3	100mg+500mg+2gm +X+V+U+S+Q+TARE +200mg/2	297.15	0.74735	298.71	5.4663
4	100mg+200mg+ +200*mg+500mg +1gm+2gm+X+S +TARE	297.25	0.7472	299.26	3.8225
	2gm+O+N+M+J+H +G+D+C+B+A +TARE	297.45	0.7467	299.82	1.8617
	1gm+O+L+K+I+G +A+TARE	297.55	0.7476	299.71	1.3018

Ex- pan- sion	DWG/APG weights Designation	Gauge Temp. K	Barometric pressure Meter of mercury	Barometric temp. K	Corrected pressure Bars
8 ^a	500mg+O+M+K+J +E+D+C+B+A +TARE	298.55	0.7476	299.71	0.9032
9	O+L+K+J+G+C+B +A+TARE	298.35	0.74635	299.54	0.6312
10	500mg+2gm+N+M+K +G+B+A+TARE	297.95	0.7464	298.98	0.4402
T = 373.15 K					
0	200*mg+200*mg +200mg+500mg+R +Q+P+O+TARE+ 100mg/2	296.55	0.7535	298.15	16.1645
1	100mg+200*mg +200mg+500mg+V +U+T+S+O+TARE	297.95	0.7555	298.26	11.2812
2	200mg+1gm+X+V+U +T+S+P+TARE	296.35	0.75435	297.71	7.8747
3	500mg+T+S+R +TARE	297.85	0.75555	299.54	5.4990

Ex- pan- sion	DWG/APG weights Designation	Gauge Temp. K	Barometric pressure Meter of mercury	Barometric temp. K	Corrected pressure Bars
4	100mg+500mg+W +S+TARE+200mg/2	298.35	0.7543	299.37	3.8466
5					
6	M+L+K+H+G+D+C +B+A+TARE	298.50	0.75375	299.15	1.8634
7	M+L+K+I+G+A+ +TARE	299.00	0.7516	299.25	1.3100
8 ^a	O+J+I+E+D+C+B+A +TARE	299.90	0.7520	298.59	0.9272
9	1gm+O+N+I+G+C+B +A+TARE	298.65	0.75215	297.30	0.6365
10	N+G+B+A+TARE	298.25	0.75215	298.15	0.4291
T = 393.15 K					
O	100mg+200mg +500mg+1gm+P+N +TARE+50mg/2	297.55	0.7492	298.98	20.2904
1	100mg+200mg+2gm +2*gm+X+S+P+O +TARE	297.75	0.74975	299.21	14.1482

Ex- pan- sion	DWG/APG weights Designation	Gauge Temp. K	Barometric pressure Meter of mercury	Barometric temp. K	Corrected pressure Bars
2	100mg+500mg+1gm +2gm+X+W+V+T +R+Q+P+TARE	298.35	0.7501	299.54	9.87879
3	200mg+1gm+5gm +T+P+TARE +100mg/2	298.55	0.74965	299.93	6.9007
4	200mg+200*mg+2gm +2*gm+T+Q+TARE	298.15 K	0.7485	300.82	4.8245
5	500mg+1gm+2gm +V+U+TARE	298.55	0.7478	300.15	3.3731
6					
7	1gm+O+N+K+I+G +C+B+A+TARE	296.95	0.7484	298.71	1.6433
8	500mg+O+L+K+J +I+G+TARE	297.35	0.74855	298.43	1.1495
9 ^a	500mg+O+N+K+J+G +D+C+B+A+TARE	297.65	0.74925	298.87	0.7983
10	500mg+O+N+K+J+C +B+A+TARE	297.95	0.7490	299.82	0.5574

Ex- pan- sion	DWG/APG weights Designation	Gauge Temp. K	Barometric pressure Meter of mercury	Barometric temp. K	Corrected pressure Bars
T = 413.15 K					
0	200mg+200*mg +500mg+1gm+X+V +T+P+N+TARE +100mg/2	299.15	0.7471	300.37	15.9352
1	200mg+200*mg +1gm+W+T+S+P +O+TARE +100mg/2	298.55	0.7492	300.37	11.2052
2	100mg+200mg +5gm+V+O+TARE	298.65	0.7496	299.82	7.8239
3	100mg+500mg 1gm+W+V+T+P +TARE	298.25	0.7486	299.82	5.4663
4	200mg+200*mg +500mg+1gm +V+T+Q+TARE	297.55	0.74835	300.21	3.8225
5	100mg+500mg +X+T+TARE	297.85	0.74915	299.82	1.8617

Ex- pan- sion	DWG/APG weights Designation	Gauge Temp. K	Barometric pressure Meter of mercury	Barometric temp. K	Corrected pressure Bars
7	1gm+O+N+L+K+H +G+C+B+A+TARE	297.75	0.7494	299.37	1.3018
8	2gm+N+K+J+H +G+TARE	298.65	0.7493	299.37	0.9032
9 ^a	2gm+O+N+M+K+I +G+D+C+B+A +TARE	299.05	0.7513	300.93	0.6312
10	500mg+O+K+I+C +B+A+TARE	299.95	0.7482	301.48	0.4401

APPENDIX F

EXPERIMENTAL PRESSURE AND TEMPERATURE DATA FOR REFRIGERANT 50C

Expansion	DWG/APG Weights Designation	Gauge Temp. K	Barometric pressure Meter of Mercury	Barometric Temperature K	Corrected Pressure Bars
0	100mg+200mg+5mg +X+U+T+S+Q+TARE +200*mg/2	T = 298.15 K 295.15	RUN 1 0.7531	298.98	5.6963
1	2gm+T+S+TARE +200mg/2	296.65	0.75295	299.26	4.1287
2					
3	500mg+1 gm+20*gm +O+N+M+L+K+J+I+H +G+E+D+C+B+A+TARE	297.35	0.7526	298.98	2.0953
4	2gm+O+N+L+K+I+G+B +A+TARE	297.15	0.7513	298.71	1.4823
5	2gm+O+N+M+K+J +TARE	297.45	0.75075	299.26	1.0481
6 ^a	1 gm+N+K+J+D+C+B +A+TARE	297.85	0.7509	300.37	0.7286

TARE denotes total mass of the tare components of piston gauge assembly.

- a Denotes that pressure from expansion no. 6 and onwards has been measured with reference to a pressure of 6.8×10^{-4} bars.

Ex- pan- sion	DWG/APG Weights Designation	Gauge Temp. K	Barometric pressure Meter of Mercury	Barometric Temperature K	Corrected Pressure Bars
7	1gm+N+L+K+H+G +B+A+TARE	298.65	0.75095	300.65	0.5120
8	O+N+L+K+J+H+G +A+TARE	297.45	0.7503	299.82	0.3577
		T = 298.15 K	RUN 2		
0	100mg+1gm+5gm +X+U+V+Q+R +TARE+200mg/2	296.25	0.7483	297.48	6.1758
1	1gm+X+Q+TARE +200mg/2	296.75	0.7475	298.15	4.4938
2	100mg+500mg +2gm+V+TARE +200mg/2	297.15	0.7476	299.26	3.2305
3					
4	1gm+N+M+J+G+C +B+A+TARE	296.75	0.74875	298.98	1.6223
5	O+M+K+J+I+G +TARE	296.65	0.74935	299.82	1.1472
6 ^a	2gm+M+K+J+G+D +C+B+A+TARE	298.15	0.7474	300.93	0.7996

Ex- pan- sion	DWG/APG Weights Designation	Gauge Temp. K	Barometric pressure Meter of mercury	Barometric Temp. K	Corrected pressure Bars
7	L+K+J+C+B+A +TARE	296.65	0.74825	300.37	0.5616
8	1gm+O+N+L+K +J+B+A+TARE	296.95	0.7482	298.15	0.3924
9	1gm+N+J+G+A +TARE	298.15	0.74835	300.93	0.2745
10	1gm+N+M+I+H +G+TARE	298.15	0.74815	299.26	0.1919
T = 298.15 K RUN 3					
0	200mg+X+W+V +T+Q+TARE +200*mg/2	297.05	0.7518	299.26	5.0457
1	1gm+W+V+T +TARE+200mg/2	297.25	0.7517	299.76	3.6397
2					
3	2gm+M+K+J+I +G+D+C+B+A +TARE	296.95	0.7555	298.71	1.8431
4	1gm+O+N+M+I +G+A+TARE	297.15	0.7500	297.59	1.2977

Ex- pan- sion	DWG/APG Weights Designation	Gauge Temp. K	Barometric pressure Meter of mercury	Barometric Temp. K	Corrected pressure Bars
5 ^a	2gm+L+K+J+E+D +C+B+A+TARE	297.85	0.7528	300.93	0.9063
6	2gm+N+I+G+C+B +A+TARE	298.45	0.7525	301.04	0.6361
7	2gm+N+J+G+B+A +TARE	298.65	0.7511	300.93	0.4469
8	0+N+M+J+I+G+A +TARE	297.75	0.7509	299.26	0.3130
9	2gm+L+K+J+A +TARE	297.95	0.75255	300.82	0.2180
10	2gm+O+N+L+K+J +I+H+TARE	298.95	0.7521	300.93	0.1518
T = 313.15 K RUN 1					
0	500mg+2gm+2*gm +V+S+P+TARE 200mg/2	297.55	0.7502	299.82	7.3734
1	2gm+W+U+S+Q +TARE+200mg/2	297.45	0.7503	299.43	5.3637
2	100mg+500mg+2gm +W+S+TARE +200mg/2	297.65	0.75165	299.82	3.8553

Ex- pan- sion	DWG/APG Weights Designation	Gauge Temp. K	Barometric pressure Meter of mercury	Barometric Temp. K	Corrected pressure Bar
3					
4	2gm+O+K+J+I+E +D+C+B+A+TARE	297.45	0.75195	300.21	1.9393
5	1gm+N+M+B+A +TARE	297.85	0.7516	299.82	1.3682
6 ^a	1gm+N+M+K+G+E +D+C+B+A+TARE	298.35	0.75205	298.71	0.9559
7	1gm+N+H+G+C+B +A+TARE	297.25	0.75345	299.26	0.6703
8	1gm+O+K+I+G+B +A+TARE	298.85	0.7532	300.93	0.4693
9	NH+H+G+A+TARE	298.95	0.75235	300.93	0.3293
10	2gm+O+K+I+A +TARE	298.45	0.7520	299.54	0.2292
T = 313.15 K RUN 2					
0	500mg+X+W+V+T +S+Q+TARE	297.95	0.7519	299.82	5.7350
1	500mg+2gm+T+S +TARE+200mg/2	296.95	0.7528	299.37	4.1314

Ex- pan- sion	DWG/APG Weights Designation	Gauge Temp. K	Barometric pressure Meter of mercury	Barometric Temp. K	Corrected pressure Bars
2					
3	O+L+K+J+I+H +G+E+D+C+B+A +TARE	297.15	0.75155	298.98	2.0825
4	N+M+I+G+B+A +TARE	297.65	0.75125	298.98	1.4705
5	N+K+J+TARE	298.15	0.75065	299.26	1.0431
6 ^a	2gm+O+J+D+C +B+A+TARE	297.55	0.7520	298.71	0.7213
7	1gm+O+N+K+H +G+B+A+TARE	296.45	0.75135	298.15	0.5060
8	O+N+M+K+J+H +G+A+TARE	298.15	0.7496	299.82	0.3542
9	O+N+K+J+I+A +TARE	298.65	0.74975	300.37	0.2476
T = 313.15 K RUN 3					
0	500mg+1gm+5gm +X+W+V+T+R+Q +TARE	297.55	0.75065	299.26	6.4562

Ex- pan- sion	DWG/APG Weights Designation	Gauge Temp. K	Barometric pressure Meter of mercury	Barometric temperature K	Corrected pressure Bars
1	200mg+200*mg +500mg+W+V+R +TARE	297.65	0.7508	299.43	4.6694
2	200mg+200*mg +1gm+2gm+X+W+V +TARE	297.45	0.7509	298.71	3.3423
3					
4	1gm+O+N+H+G+C +B+A+TARE	296.75	0.74955	299.37	1.6724
5	2gm+O+N+K+J+H +G+TARE	297.35	0.7493	299.76	1.1804
6 ^a	2gm+O+N+L+K+I +G+D+C+B+A +TARE	297.85	0.7507	299.71	0.8228
7	2gm+O+M+K+I+C +B+A+TARE	297.35	0.7500	298.71	0.5768
8	1gm+M+K+I+B+A +TARE	297.95	0.7493	299.82	0.4036
9	O+N+K+J+G+A +TARE	297.05	0.7505	299.26	0.2820
10	M+K+A+TARE	296.95	0.74955	297.43	0.1968

Ex- pan- sion	DWG/APG Weights Designation	Gauge Temp. K	Barometric pressure Meter of mercury	Barometric temperature K	Corrected pressure Bars
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T = 333.15 K RUN 1

0	100mg+200mg +200*mg+500mg +1gm+2gm+T+P +TARE+200*mg/2	297.95	0.7454	299.82	6.8825
1	100mg+1gm+2gm +V+T+R+TARE +200mg/2	298.15	0.7463	299.82	4.9519
2	200mg+500mg+1gm +X+W+T+TARE 100mg/2	297.35	0.7461	299.71	3.5328
3					
4	O+N+M+J+I+D+C +B+A+TARE	297.65	0.7494	298.15	1.7612
5	2gm+O+J+I+A +TARE	297.45	0.74905	299.09	1.2402
6 ^a	1gm+K+J+H+G+D +C+B+A+TARE	297.95	0.7550	300.32	0.8647
7	1gm+O+N+M+G+C +B+A+TARE	297.95	0.75195	299.82	0.6057

Ex- pan- sion	DWG/APG Weights Designation	Gauge Temp. K	Barometric pressure Meter of mercury	Barometric temperature K	Corrected pressure Bars
8	L+K+J+I+B+A +TARE	295.95	0.7529	298.26	0.4239
9	K+I+G+A+TARE	296.95	0.7512	299.26	0.2966
10	2gm+O+N+J+A +TARE	297.65	0.7504	298.43	0.2069
T = 333.15 K ; RUN 2					
0	200mg+500mg+1gm +X+V+U+Q+R+TARE	297.05	0.7504	299.09	6.1528
1	100mg+2gm+2*gm +V+U+T+S+TARE	297.25	0.7505	298.71	4.4121
2	200mg+2gm+2*gm +X+TARE	297.05	0.7510	298.26	3.1405
3					
4	2gm+O+N+M+J+C +B+A+TARE	296.85	0.7518	298.82	1.5587
5	M+K+G+TARE	297.35	0.7516	298.93	1.0976
6 ^a	O+N+K+J+I+D+C +B+A+TARE	296.85	0.7495	299.26	0.7634
7	1gm+O+M+C+B+A +TARE	297.65	0.7488	299.26	0.5352

Ex- pan- sion	DWG/APG Weights Designation	Gauge Temp. K	Barometric pressure Meter of mercury	Barometric temperature K	Corrected pressure Bars
8	N+L+K+B+A +TARE	297.75	0.74875	299.37	0.3740
9	1gm+O+N+M+G +A+TARE	297.85	0.7491	298.15	0.2616
T = 333.15 K RUN 3					
0	200mg+200*mg +1gm+2gm+W+T+S +R+TARE	297.35	0.7495	299.15	5.5767
1	500mg+2gm+W+V +S+TARE	297.35	0.74925	298.59	3.9883
2					
3	1gm+N+M+K+I+G +E+D+C+B+A +TARE	296.65	0.7467	299.26	1.9877
4	1gm+O+N+K+I+B +A+TARE	297.25	0.74675	299.26	1.4003
5 ^a	1gm+N+L+K+J+G +E+D+C+B+A +TARE	297.85	0.7472	299.26	0.9765

Ex- pan- sion	DWG/APG Weights Designation	Gauge Temp. K	Barometric pressure Meter of mercury	Barometric temperature K	Corrected pressure Bars
6	2gm+O+N+L+K+H +G+C+B+A+TARE	297.45	0.74725	299.82	0.6852
7	2gm+J+I+G+B+A +TARE	298.05	0.7466	299.82	0.4796
8	1gm+O+M+K+H+G +A+TARE	298.65	0.74765	300.37	0.3356
9	1gm+O+N+M+K+I +A+TARE	298.75	0.74875	300.37	0.2341
T = 353.15 K RUN 1					
0	200mg+200*mg +5gm+X+W+T+P TARE	297.75	0.7474	300.37	6.9961
1	100mg+200mg +500mg+W+V+T +R+TARE	296.95	0.7470	300.82	5.0080
2	200mg+V+T+TARE	297.95	0.74695	299.82	3.5593
3					
4	500mg+O+L+K+J +I+D+C+B+A +TARE	297.45	0.7484	300.82	1.7690

Ex- pan- sion	DWG/APG Weights Designation	Gauge Temp. K	Barometric pressure Meter of mercury	Barometric temperature K	Corrected pressure Bars
5	2gm+N+M+J+I+A +TARE	297.55	0.74825	298.71	1.2434
6 ^a	1gm+N+K+J+H+G +D+C+B+A+TARE	297.95	0.74935	298.32	0.8664
7	1gm+K+G+C+B+A +TARE	298.85	0.7478	300.54	0.6066
8	2gm+L+K+J+I+B +A+TARE	298.95	0.74835	300.10	0.4245
9	2gm+O+N+M+I+G +A+TARE	298.85	0.74815	300.32	0.2963
10	1gm+M+J+A+TARE	298.05	0.74805	299.43	0.2074
T = 353.15 K RUN 2					
0	500mg+2gm+2*gm +V+T+Q+R+TARE	298.05	0.74935	301.20	6.3399
1	100mg+200mg +200*mg+500mg +W+Q+TARE +200*mg/2	297.85	0.74665	300.65	4.5276
2	200mg+500mg+5gm +W+X+TARE	297.35	0.74695	299.82	3.2120

Ex- pan- sion	DWG/APG Weights Designation	Gauge Temp. K	Barometric pressure Meter of mercury	Barometric temperature K	Corrected pressure Bars
3					
4	2gm+N+M+K+J+I +C+B+A+TARE	297.65	0.74695	299.82	1.5928
5	N+M+I+G+TARE	296.35	0.74645	300.37	1.1202
6 ^a	O+K+G+D+C+B +A+TARE	297.55	0.74745	298.15	0.7792
7	500mg+2gm+O+L +K+C+B+A+TARE	298.45	0.7482	300.93	0.5459
8	O+N+M+J+B+A +TARE	298.85	0.7486	301.20	0.3818
9	2gm+O+M+K+G+A +TARE	298.95	0.7475	301.31	0.2671
10	1gm+O+N+L+K+J +H+G+TARE	298.90	0.7474	298.15	0.1859
T = 353.15 K RUN 3					
0	100mg+200mg +1gm+5gm+W+T +S+Q+TARE	299.25	0.7571	301.48	5.6040

Ex- pan- sion	DWG/APG Weights Designation	Gauge Temp. K	Barometric pressure Meter of mercury	Barometric temperature K	Corrected pressure Bars
1	200mg+200*mg 500mg+1gm+W+V +S+TARE+100mg/2	298.65	0.7464	301.53	3.9819
2					
3	2gm+O+N+M+I+G +E+D+C+B+A +TARE	298.40	0.74645	301.42	1.9820
4	2gm+M+I+B+A +TARE	298.85	0.7467	298.71	1.3944
5 ^a	1gm+O+M+K+J+G +E+D+C+B+A +TARE	299.58	0.74825	301.20	0.9722
6	1gm+O+N+M+K +H+G+C+B+A +TARE	299.65	0.7483	300.93	0.6814
7	N+L+K+I+G+B+A +TARE	297.05	0.7485	299.99	0.4773
8	M+K+H+G+A+TARE	298.55	0.7465	298.71	0.3345
9	1gm+N+M+K+I+A +TARE	297.85	0.7468	298.15	0.2332

Ex- pan- sion	DWG/APG weights Designation	Gauge Temp. K	Barometric pressure Meter of mercury	Barometric temperature K	Corrected pressure Bars
T = 373.15 K RUN 1					
0	100mg+200mg+1gm +2gm+2*gm+X+T+P +TARE	298.05	0.74695	299.82	6.9260
1	200mg+500mg+5gm +X+W+T+Q+TARE	298.55	0.7486	298.71	4.9351
2	500mg+2gm+5gm +X+T+TARE	298.05	0.74815	299.82	3.5000
3					
4	O+M+K+J+D+C+B +A+TARE	297.85	0.74885	297.59	1.7311
5	500mg+1gm+O+M+K +J+A+TARE	297.45	0.7501	298.04	1.2172
6 ^a	2gm+O+N+M+H+G+D +C+B+A+TARE	298.75	0.7500	298.26	0.8469
7	2gm+O+M+K+J+I +C+B+A+TARE	298.85	0.74995	299.26	0.5940
8	1gm+O+M+J+I+B +A+TARE	298.45	0.74865	298.98	0.4143

Ex- pan- sion	DWG/APG weights Designation	Gauge Temp. K	Barometric pressure Meter of mercury	Barometric temperature K	Corrected pressure Bars
9	2gm+I+G+A +TARE	297.35	0.7511	298.15	0.2903
10	O+N+L+K+A +TARE	297.35	0.75125	297.70	0.2028
T = 373.15 K RUN 2					
0	100mg+200mg +500mg+1gm+2gm +V+U+Q+R+TARE +200*mg/2	297.85	0.7521	299.26	6.1334
1	100mg+200mg +500mg+X+W+V+T +S+TARE	297.75	0.75155	298.15	4.3600
2	200mg+1gm+TARE	298.25	0.75095	299.82	3.0888
3					
4	1gm+O+N+K+J+H +G+B+A+TARE	297.85	0.74905	298.15	1.5236
5	M+J+I+TARE	297.85	0.74905	297.59	1.0699
6 ^a	500mg+2gm+K+I +D+C+B+A+TARE	297.75	0.7502	298.15	0.7447

Ex- pan- sion	DWG/APG weights Designation	Gauge Temp. K	Barometric pressure Meter of mercury	Barometric temp. K	Corrected pressure Bars
7	1gm+K+J+H+G+B +A+TARE	297.65	0.7499	297.87	0.5206
8	500mg+2gm+N+M+B +A+TARE	297.85	0.7488	300.37	0.3644
9	0+N+L+K+J+I+A +TARE	297.85	0.7484	298.71	0.2545
T = 373.15 K RUN 3					
0	200mg+500mg+5gm +T+S+Q+TARE	297.75	0.7495	298.65	5.5211
1	200mg+500mg+2gm +V+S+TARE	297.55	0.7494	298.15	3.9209
2					
3	500mg+1gm+M+G +E+D+C+B+A +TARE	297.75	0.74695	298.71	1.9451
4	500mg+2gm+M+K +B+A+TARE	298.05	0.74685	298.54	1.3672
5 ^a	500mg+2gm+N+K+G +E+D+C+B+A+TARE	298.35	0.74855	298.71	0.9528
6	0+N+L+K+J+I+G+C +R+A+TARE	297.35	0.7496	298.71	0.6674

Ex- pan- sion	DWG/APG weights Designation	Gauge Temp. K	Barometric pressure Meter of mercury	Barometric temp. K	Corrected pressure Bars
7	500mg+N+M+I+G +B+A+TARE	298.55	0.74765	299.26	0.4671
8	2gm+N+H+G+A +TARE	298.05	0.74925	298.26	0.3264
9	500mg+2gm+K+I +A+TARE	298.65	0.7495	298.71	0.2285
T = 393.15 K RUN 1					
0	100mg+1gm+2gm +5gm+X+V+T+P +TARE	298.65	0.7479	300.93	7.0811
1	100mg+500mg+2gm +2*gm+W+V+T+Q +TARE	299.35	0.7478	299.26	5.0307
2	200mg+200*mg +500mg+5gm+X+W+T +TARE	298.75	0.74825	298.71	3.5596
3					
4	500mg+O+N+J+I+D+C +B+A+TARE	298.35	0.74935	300.10	1.7581
5	1gm+O+L+K+I+A +TARE	299.35	0.74785	299.82	1.2350

Ex- pan- sion	DWG/APG weights Designation	Gauge Temp. K	Barometric pressure Meter of mercury	Barometric temp. K	Corrected pressure Bars
6 ^a	500mg+1gm+N+J +H+G+D+C+B+A +TARE	299.35	0.7484	300.82	0.8596
7	500mg+1gm+N+G+C +B+A+TARE	298.85	0.7474	300.10	0.6016
8.	500mg+1gm+M+K+J +I+B+A+TARE	299.25	0.74855	300.26	0.4209
9.	500mg+O+M+I+G+A +TARE	297.95	0.7484	298.99	0.2942
T = 393.15 K RUN 2					
0	1gm+2gm+2*gm+W +T+R+Q+TARE	298.05	0.74905	298.43	6.2731
1	200mg+1gm+2gm +2*gm+X+V+U+T +S+TARE	297.05	0.74925	298.03	4.4513
2	100mg+200mg +500mg+5gm+X +TARE	297.95	0.74925	298.98	3.1475

Ex- pan- sion	DWG/APG weights Designation	Gauge Temp. K	Barometric pressure Meter of mercury	Barometric temp. K	Corrected pressure Bars
4	500mg+1gm+O +N+M+J+C+B+A +TARE	297.65	0.7469	299.26	1.5520
5	N+K+G+TARE	298.25	0.74685	298.77	1.0895
6 ^a	2gm+M+J+I+D +C+B+A+TARE	295.95	0.7475	297.32	0.7583
7	500mg+C+B+A+TARE	298.35	0.7474	300.37	0.5307
8	500mg+N+M+K+B +A+TARE	297.95	0.74695	299.26	0.3707
9	500mg+M+G+A +TARE	298.75	0.75025	300.10	0.2589
T = 393.15 K RUN 3					
0	100mg+2gm+V+T +S+Q+TARE	298.05	0.7471	299.82	5.6346
1	200mg+200*mg +1gm+2gm+W+V+S +TARE+100mg/2	299.05	0.7476	299.82	3.9919
2					
3	L+K+J+G+E+D+C +B+A+TARE	299.15	0.7484	299.26	1.9742

Ex- pan- sion	DWG/APG weights Designation	Gauge Temp. K	Barometric pressure Meter of mercury	Barometric temp. K	Corrected pressure Bars
4	O+N+K+J+B+A +TARE	298.85	0.7502	300.82	1.3877
5 ^a	O+N+M+J+G+E +D+C+B+A +TARE	298.95	0.74775	300.10	0.9667
6	500mg+2gm+O+K+H +G+C+B+A+TARE	298.75	0.7480	299.26	0.6767
7	O+M+K+I+G+B+A +TARE	297.55	0.74835	298.71	0.4730
8.	1gm+K+H+G+A +TARE	298.75	0.74765	298.88	0.3313
T = 413.15 K RUN 1					
0	200mg+200*mg +1gm+X+T+P +TARE	300.25	0.7460	301.48	6.9022
1	100mg+200mg +200*mg+2gm +2*gm+W+T+Q +TARE	298.95	0.7481	301.48	4.8934

Ex- pan- sion	DWG/APG weights Designation	Gauge Temp. K	Barometric pressure Meter of mercury	Barometric temp. K	Corrected pressure Bars
2	100mg+200mg +500mg+5gm+T +TARE	299.15	0.7482	300.65	3.4560
3					
4	O+D+C+B+A +TARE	299.25	0.7481	300.37	1.7030
5	1gm+N+K+A +TARE	299.45	0.74825	300.37	1.1952
6 ^a	2gm+N+K+J+I +G+D+C+B+A +TARE	301.55	0.74935	302.59	0.8322
7	500mg+1gm+O +N+L+K+I+C+B +A+TARE	301.95	0.7487	303.48	0.5817
8	2gm+L+K+I+B +A+TARE	301.95	0.7476	302.87	0.4073
9	500mg+2gm+O+M +K+J+G+A+TARE	300.95	0.74655	301.48	0.2844

Ex- pan- sion	DWG/APG weights Designation	Gauge Temp. K	Barometric pressure Meter of mercury	Barometric temp. K	Corrected pressure Bars
0	200mg+200*mg +2gm+V+U+T+S +Q+TARE	T= 413.15 K 300.35	RUN 2 0.74675	301.37	5.7738
1	200mg+500mg +1gm+X+V+U+S +TARE+200mg/2	299.55	0.74705	300.65	4.0850
2					
3	2gm+K+H+G+E +D+C+B+A+TARE	299.75	0.74695	301.04	2.0178
4	N+K+J+I+B+A +TARE	300.35	0.7469	300.76	1.4167
5 ^a	O+N+K+I+G+E +D+C+B+A+TARE	300.95	0.74815	302.04	0.9873
6	500mg+1gm+N+M+J +H+G+C+B+A+TARE	300.95	0.74635	302.92	0.6910
7	1gm+O+M+J+I+G+B +A+TARE	300.35	0.7467	302.59	0.4836
8	1gm+L+K+H+G+A +TARE	299.65	0.7475	301.04	0.3382

APPENDIX G

MATERIALS USED

Helium

Helium of 99.99 mole% purity was obtained from the Low Temperature Laboratory, Indian Institute of Technology, Kanpur. The purity was checked by Gas-Liquid chromatography and was found to comply with the above specifications.

Refrigerant 500

Refrigerant 500 used was of 99.95 mole % stated purity made by DuPont de Nemours, and was supplied by the Universal Commercial Company, Bombay. It was used without further purification. The selected physical properties and the ideal gas thermodynamic functions are reported in Appendices H and I respectively.

APPENDIX H

PHYSICAL PROPERTIES OF REFRIGERANT 500

Critical Constants: $T_c = 378.20 \text{ K}$, $P_c = 43.51 \text{ bars}$

Freezing point = 114.26 K Boiling point = 239.85 K

Molecular weight = 99.31

Temp., K	Density, m^3/Kg	Temp., K	Vapour Pressure Bars
212.83	5.468	183.29	0.4656
250.75	5.074	228.18	0.5959
284.86	4.676	237.10	0.8998
313.47	4.287	253.16	1.8938
337.00	3.893	263.20	2.5821
354.66	3.503	273.15	3.624
366.92	3.114	294.59	6.9636
		313.07	11.3417
		333.17	18.0916
		353.12	27.3442
		373.17	39.7752

APPENDIX I

IDEAL GAS THERMODYNAMIC PROPERTIES FOR REFRIGERANT 500

$\frac{T}{K}$	$\frac{C_p^O}{JK^{-1}mole^{-1}}$	$\frac{S^O}{JK^{-1}mole^{-1}}$	$\frac{-(G^O-H_O^O)/T}{JK^{-1}mole^{-1}}$	$\frac{(H^O-H_O^O) \times 10^{-1}}{Jmole^{-1}}$
O	O	O	O	O
100.00	39.3184	241.2762	206.6160	3.4660
150.00	47.9972	258.8465	221.1855	5.6484
200.00	56.3928	273.8252	232.5266	8.2596
273.15	67.2775	293.0490	246.2209	12.7934
298.15	70.6615	299.0765	250.3898	14.5181
300.00	70.9037	299.5200	250.7078	14.6486
400.00	82.7784	321.6157	265.7338	22.3568
500.00	92.0020	341.1152	278.8829	31.1147
600.00	99.0842	358.5424	290.7324	40.6844
700.00	104.6130	374.2500	301.5589	50.8812
800.00	109.0237	388.5162	311.5637	61.5713
900.00	112.5927	401.6828	320.8304	72.6543
1000.00	115.5290	413.5880	329.5356	84.0666
1100.00	117.9746	424.6973	337.6957	95.7421
1200.00	120.0791	435.0937	345.3792	107.6472
1300.00	121.7778	444.7546	352.6187	119.7578
1400.00	120.8394	453.8958	359.6048	132.0144
1500.00	124.6179	462.4031	366.0582	144.4166

Thermodynamic properties of mixture of R 12 (say, A) and R 152 a (say, B) are obtained from the ideal gas thermodynamic functions of the two constituents.

Heat capacity of the mixture

$$C_P^O = x_A C_{P_A}^O + x_B C_{P_B}^O$$

where C_P is specific heat at constant pressure.

Enthalpy of the mixture

$$H^O - H_O^O = x_A (H^O - H_O^O)_A + x_B (H^O - H_O^O)_B$$

Entropy of the mixture

$$S^O = x_A S_A^O + x_B S_B^O - x_A \ln x_A - x_B \ln x_B$$

Gibbs energy of the mixture

$$\begin{aligned} (G^O - H_O^O)/T &= x_A (G^O - H_O^O)_A/T + x_B (G^O - H_O^O)_B/T \\ &+ x_A \ln x_A + x_B \ln x_B \end{aligned}$$

where x is the molar fraction.

APPENDIX J

AUXILIARY DATA

1. Absolute temperature of the ice point, $^{\circ}\text{C} = 273.15 \text{ K}$
2. Gas constant, $R = 1.98717 \text{ cal deg}^{-1} \text{ mole}^{-1}$
 $= 8.31441 \text{ JK}^{-1} \text{ mole}^{-1}$
 $= 82.0561 \times 10^{-6} \text{ m}^3 \text{ atm deg}^{-1} \text{ mole}^{-1}$
3. Standard gravity, $g_0 = 9.80665 \text{ m sec}^{-2}$
4. Local gravity, $g = 9.78977 \text{ m sec}^{-2}$